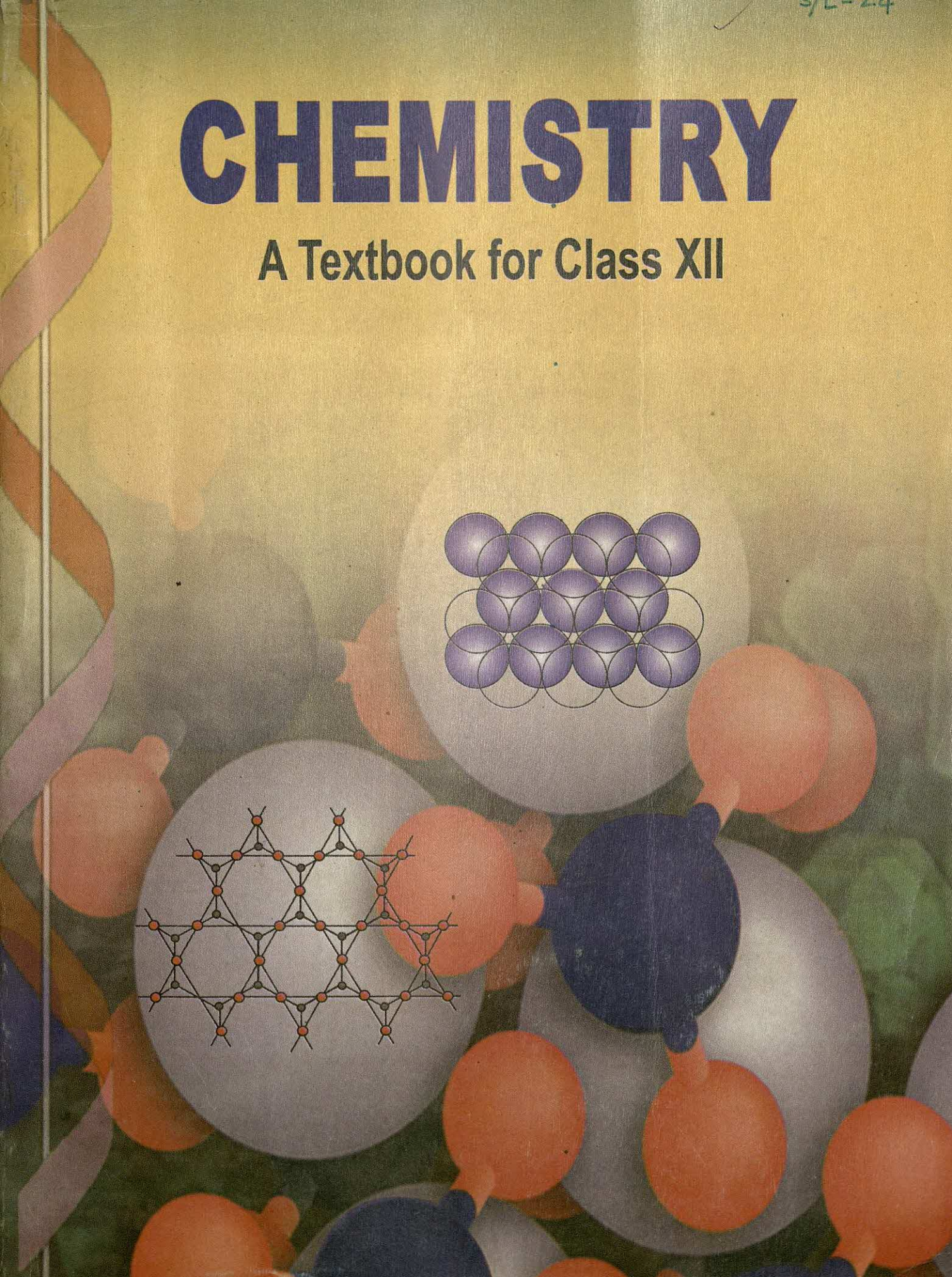
CHEMISTRY

A Textbook for Class XII



S.C.E.R.T., W.B.
N C.F, '2005

Text book
Code no. 013

CHEMISTRY

Textbook for Class XII

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N.C.E.R.T. Library
13/3, B. C. Road

राष्ट्रीय शैक्षिक अनुसंधान और प्रशिक्षण परिषद्
NATIONAL COUNCIL OF EDUCATIONAL RESEARCH AND TRAINING

S.C.E.R.T., W.B.
N.C.F.-2005

First Edition
March 2003 Phalguna 1924

Reprinted
December 2003 Agrahayana 1925
March 2005 Chaitra 1927
November 2005 Agrahayana 1927

PD 75T + 13T VJ

ISBN 81-7450-190-8

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OFFICES OF THE PUBLICATION DEPARTMENT, NCERT

NCERT Campus, Sri Aurobindo Marg, **New Delhi 110 016**
108, 100 Feet Road, Hosdakere Halli Extension, Banashankari III Stage, **Bangalore 560 085**
Navjivan Trust Building, P.O.Navjivan, **Ahmedabad 380 014**
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24.3.2008
13196

PUBLICATION TEAM

Editorial Vineet Joshi
Production Atul Saxena
Layout
Kalyan Banerjee

Rs. 140.00

Printed on 80 GSM paper with NCERT watermark

Published at the Publication Department by the Secretary, National Council of Educational Research and Training, Sri Aurobindo Marg, New Delhi 110 016 and printed at **Shagun Offset Pvt. Ltd. B-3, Sector-65, Noida (U.P.)**

PUBLISHER'S NOTE

The National Council of Educational Research and Training (NCERT) has been preparing and publishing school textbooks and other educational material for children and teachers. These publications are regularly revised on the basis of feedback from students, teachers, parents, and teacher educators. Research done by the NCERT also forms the basis for updating and revision.

This book is based on the National Curriculum Framework for School Education – 2000 and the syllabi prepared in accordance with it. The Executive Committee of the NCERT, in its meeting held on 19 July 2004, discussed all aspects related to the quality of textbooks and decided that the textbooks of all subjects should undergo a quick review. In pursuance of this decision, the NCERT constituted 23 Quick Review Committees to examine all the textbooks. These committees identified various errors of conceptual, factual and linguistic nature. The review process also took note of the evaluation of textbooks undertaken earlier. The exercise has now been completed and the errors identified have been corrected. We hope that this revised edition will serve as an effective medium of teaching and learning. We look forward to your suggestions to enable us to further improve the quality of this book.

SECRETARY
National Council of Educational
Research and Training

New Delhi
January 2005

CONSTITUTION OF INDIA

Preamble

WE, THE PEOPLE OF INDIA, having solemnly resolved to constitute India into a **SOVEREIGN SOCIALIST SECULAR DEMOCRATIC REPUBLIC** and to secure to all its citizens:

JUSTICE, social, economic and political;

LIBERTY of thought, expression, belief, faith and worship;

EQUALITY of status and of opportunity; and to promote among them all

FRATERNITY assuring the dignity of the individual and the unity and integrity of the Nation;

IN OUR CONSTITUENT ASSEMBLY this twenty-sixth day of November, 1949, do **HEREBY ADOPT, ENACT AND GIVE TO OURSELVES THIS CONSTITUTION.**

PREFACE

This textbook of Chemistry for Class XII has been written in the same format and spirit as its previous part for Class XI. Together these two volumes not only fully cover the curriculum in Chemistry for higher secondary classes in our schools but also provide enough material for an independent course of Chemistry at tertiary level or even for self-study.

Chemistry occupies a central position in the study of modern science. The well being of **Man and Society** are intimately linked to and dependent on chemistry in one way or the other. A large body of chemical information is based on the results obtained from painstaking experiments and is explained in terms of molecules, their structure and interaction amongst themselves. The subject is, therefore, both facts and concepts oriented and in this book we have tried to present it in as lucid and simple style as possible with judicious blend of facts, concepts and principles. In order to ensure easy readability, understanding and assimilation, a large number of solved examples have been incorporated in each Unit. Informative material in boxes, given throughout the book, either reveal some historical landmark in the development of the subject and biographical sketches of eminent scientists or pass on the excitement of some recent discoveries in chemical sciences. The book is adorned with a number of colour illustrations to create a pleasant visual effect and for easy comprehension. Exercises have been included at the end of each Unit to encourage the students for self-testing of their knowledge and understanding of the subject. Several appendices consisting of useful physico-chemical data have been provided and one of these includes answer to all the numerical problems given in the exercises.

It is my pleasure to thank the members of the writing team for their kind cooperation in preparing, revising and finalising the manuscript. I am also indebted to Head, Department of Education in Science and Mathematics, NCERT for supervising the design of all the illustrations and also for looking after day-to-day problems in making the manuscript pressworthy. I am extremely grateful to the Director, NCERT for extending his support in improving the quality of production of the book from every angle.

In spite of the extra care exercised in the compilation and editing of the book, there may be some errors and omissions. The users of the book are welcome to provide suggestions and also share their experience of reading the book with us. It is hoped that the book will fulfil the expectations of the readers.

D.V.S. Jain
Chairman
Writing Team

Part IV A (Article 51 A)

Fundamental Duties

Fundamental Duties – It shall be the duty of every citizen of India —

(a) to abide by the Constitution and respect its ideals and institutions, the National Flag and the National Anthem;

(b) to cherish and follow the noble ideals which inspired our national struggle for freedom;

(c) to uphold and protect the sovereignty, unity and integrity of India;

(d) to defend the country and render national service when called upon to do so;

(e) to promote harmony and the spirit of common brotherhood amongst all the people of India transcending religious, linguistic and regional or sectional diversities; to renounce practices derogatory to the dignity of women;

(f) to value and preserve the rich heritage of our composite culture;

(g) to protect and improve the natural environment including forests, lakes, rivers, wildlife and to have compassion for living creatures;

(h) to develop the scientific temper, humanism and the spirit of inquiry and reform;

(i) to safeguard public property and to abjure violence;

(j) to strive towards excellence in all spheres of individual and collective activity so that the nation constantly rises to higher levels of endeavour and achievement;

(k) who is a parent or guardian, to provide opportunities for education to his child or, as the case may be, ward between the age of six and fourteen years.

ACKNOWLEDGEMENTS

The National Council of Educational Research and Training is grateful to the members of the Writing Committee for their valuable contributions in the development of the manuscript of this textbook. The Council also expresses its gratefulness to Professor D.V.S. Jain (*Chairman*), Punjab University; Professor M.L. Dhar, *Head* (*Retd.*), Jammu University; Professor S. S. Krishnamurthy, *Chairman*, Chemical Science Division, Indian Institute of Science, Banglore; Professor A.K. Bakhshi, Delhi University; Professor A.K. Singh, IIT, Bombay; Professor Harjit Singh, Gurunanak Dev University, Amritsar; Professor Krishna Misra, University of Allahabad; Dr K.N. Upadhyay, *Head* (*Retd.*), Ramjas College, University of Delhi; Professor R.N. Ram, IIT, New Delhi; and Professor Brahm Parkash, Professor I. P. Aggarwal, Professor R. D. Shukla (*Coordinator*), DESM, NCERT, New Delhi.

The Council acknowledges the valuable contributions of the following participants of the Review Workshop in the finalisation of this book: Professor G.T. Bhandage, *Head*, DESM, RIE, Bhopal; Dr V.P. Gupta, *Reader*, RIE, Ajmer; Shri B.S. Raghavendra, *Reader*, RIE, Mysore; Professor Ranjit K. Verma, Magadh University, Bodh Gaya; Shri Rajesh Kumar Sharma, *PGT*, Jawahar Navodaya Vidyalaya, Dungrin, Himachal Pradesh; Professor Bharat Singh, *Head*, University of Allahabad; Shri Arjun Singh "PAWAR", *PGT*, J.N.V. Chhatarpur, Madhya Pradesh; Shri R.A. Verma, *Vice-Principal*, S.A.B.G.S.V Leudlo Castle, New Delhi; Smt. Rajalakshmi K., *Head*, The Mother's International School, New Delhi; Smt. Amarjeet Kaur, *PGT*, J.N.V. Jaffarpur Kalan, New Delhi; Shri S.K. Munjal, *Principal*, St. Margaret Senior Secondary School, Delhi; Shri H.C. Pande, *ADE* (*Sc.*), Gargi College Building, New Delhi; Shri Anil Kumar Sharma, *PGT*, Kendriya Vidyalaya, INA Colony, New Delhi; Professor B.L. Dubey, *Head* (*Retd.*), D.D.U. Gorakhpur University, Uttar Pradesh; Professor Narendra Nath (*Retd.*), Gorakhpur University; Smt. Surekha Agnihotri, *PGT*, Laxman Public School, New Delhi; Dr V.B. Singh, *Reader*, BHU, Varanasi; Shri N.P. Dhaka, *Principal*, Government Boys Senior Secondary School, New Kondli, Delhi; Dr Vijay Sarda, *Reader*, Zakir Husain College, New Delhi; Dr Sunita Malhotra, *Reader*, IGNOU, New Delhi; Dr Sulekh Chandra, *Reader*, Zakir Husain College, New Delhi, Shri K.K. Singh, *PGT*, Kendriya Vidyalaya No.1, Faridabad; Shri Rajan Bandiwar, *Master*, Sainik School, Rewa; Shri R.K. Sandilya, Kendriya Vidyalaya, Unnao, Uttar Pradesh; Dr S.I. Rizvi, Allahabad University; Dr P. S. Jaiswal, *Reader*, Hans Raj College, University of Delhi; Shri A.K. Ganguli, *Associate Professor*, IIT, New Delhi; Shri A. Nabeel Siddiqui, *PGT*, Government Boys Senior Secondary School No.1, R. K. Puram, New Delhi.

The Council also gratefully acknowledges the feedback and suggestions of the following members of the Quick Review Committee for the improvement of this book: Professor H.M. Chawla (*Chairman*), IIT, New Delhi; Professor Talat Aziz, IASE, Jamia Millia Islamia, New Delhi; Dr Vinod Kumar, Hans Raj College, University of Delhi; Professor Mukhtar A. Khan, *Ex-Head*, Jamia Millia Islamia, New Delhi; Smt. Preeti Gangahar, *PGT*, Springdales School, New Delhi; Dr C. Srinivas, *PGT*, Kendriya Vidyalaya, Pushp Vihar, New Delhi; Shri Narayanan Kurur, IIT, New Delhi; Dr J.L. Sharma, *Reader*, Kirori Mal College, University of Delhi; Smt. Amita Kumar, *Head*,

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Nirmalya Chakraborty, College of Art, New Delhi

UNIT 1

ATOMIC STRUCTURE AND CHEMICAL BONDING

OBJECTIVES

After studying this Unit, you will be able to:

- understand the dual behaviour of matter and radiation, the de Broglie relationship and the Heisenberg uncertainty principle.
- know about the salient features of the quantum-mechanical model of atom, atomic orbitals and their pictorial representations, the importance of quantum numbers including magnetic spin quantum number.
- write the electronic configuration of atoms.
- understand the molecular orbital theory of chemical bonding, bonding and antibonding molecular orbitals and energy level diagrams of homonuclear diatomic molecules.
- know about the hybridizations involving *s*, *p* and *d* orbitals.
- understand the nature of metallic bonding and different types of intermolecular forces.

"If, in some cataclysm, all scientific knowledge were to be destroyed and only one sentence is passed on to the next generation.. I believe it is .. that all things are made of atoms." -Richard Feynman

You have studied the Thomson, Rutherford and Bohr models of the structure of atom in Class XI. Bohr model of the hydrogen atom was the first atomic model based on the quantisation of energy. Bohr postulated that in hydrogen atom, electron moves around the nucleus only in certain circular orbits, each corresponding to a specific energy. Bohr model, though offering a satisfactory model for explaining the spectra of the hydrogen atom and hydrogen-like ions (i.e., one electron systems), could not explain the spectra of multielectron atoms. Further, Bohr model did not provide any answer for the electronic structure of atoms i.e., the distribution of electrons in the atom. The main challenge to the Bohr model came from two discoveries: (i) the wave nature of electron; and (ii) Heisenberg uncertainty principle which states that it is impossible to determine simultaneously both the position and momentum of an electron. The first questions the specification of the position of an electron if it behaves as a wave, and the second negates the idea of movement of electron in definite paths (orbits). A new model of the structure of atom, known as the **quantum mechanical model**, was therefore proposed. This model in which the behaviour of an electron is described by a wave function, takes into account the wave-particle duality of electron and is consistent with the Heisenberg uncertainty principle. In this Unit we shall study some aspects of the quantum mechanical model.

1.1 DUAL NATURE OF MATTER AND RADIATION

Newton regarded light as a beam of particles called corpuscles. This view of the nature of light

was however discarded when interference and diffraction effects were observed with light under suitable conditions. Since such effects can only be explained on the basis of wave theory, light began to be regarded as a wave phenomena.

In the later part of the 19th century and in the beginning of the 20th century, it was realised that black body radiation and the photoelectric effect, which you have already studied in Class XI, can be understood only on the basis of a particle-model of light. Thus, some experiments require light to be a wave while others require light to be a particle. This led to the acceptance of dual (particle and wave) nature of light.

In analogy with the behaviour of light, **de Broglie** proposed that all material particles should also show dual behaviour. The particle character of matter, e.g., electron had been established from a number of experiments and its wave character was confirmed by diffraction and interference experiments. Many modern instruments like electron microscope are based on the wave nature of electrons. Neutrons, protons, hydrogen atoms and even C_{60} fullerene molecules have also been shown to possess wave character.

1.1.1 The de Broglie Relation

The French physicist Louis de Broglie in 1924 postulated that **matter, like radiation, should exhibit a dual behaviour.** He proposed the following relationship between the wavelength λ of a material particle, its linear momentum p and Planck constant h.

$$\lambda = \frac{h}{p} = \frac{h}{mv} \qquad (1.1)$$

The de Broglie relation implies that the wavelength of a particle should decrease as its velocity increases. It also implies that for a given velocity heavier particles should have shorter wavelength than lighter particles. In the case of macroscopic objects such as a bullet or a ball, the de Broglie wavelength is so small that it cannot be measured by any known means.

The waves associated with particles in motion are called **matter waves** or **de Broglie waves**. These waves differ from the electromagnetic waves as they i) have lower velocities, ii) have no electrical and magnetic fields and iii) are not emitted by the particle under consideration.

The experimental confirmation of the de Broglie relation was obtained when Davisson and Germer, in 1927, observed that a beam of electrons is diffracted by a nickel crystal[1]. **The wavelengths of the electrons determined by the diffraction experiments were found to be in agreement with the values predicted by the de-Broglie relation**. The diffraction pattern of electrons by crystals is similar to that observed for X-rays (Fig. 1.1).

Example 1.1
Calculate the de Broglie wavelength of an electron travelling at 1% of the speed of light.

Solution

The mass of an electron is 9.11×10^{-31} kg. One percent of the speed of light is

$v = (1/100)(3.00 \times 10^{8}\ \text{m s}^{-1})$
$= 3.00 \times 10^{6}\ \text{m s}^{-1}$

The momentum of the electron is given by

$p = mv = (9.11 \times 10^{-31}\ \text{kg})\ (3.00 \times 10^{6}\ \text{m s}^{-1})$
$= 2.733 \times 10^{-24}\ \text{kg m s}^{-1}$

The de Broglie wavelength of this electron is

$$\lambda = \frac{h}{p} = \frac{6.626 \times 10^{-34}\ \text{J s}}{2.733 \times 10^{-24}\ \text{kg m s}^{-1}}$$

$= 2.424 \times 10^{-10}\ \text{m} = 242.4\ \text{pm}$

This wavelength is of atomic dimensions.

1.2 HEISENBERG UNCERTAINTY PRINCIPLE

This important principle states that: **It is impossible to determine simultaneously both the position and momentum of an object with certainty. It acquires significance when applied to elementary particles.** This principle is the consequence of dual behaviour of matter and radiation.

Mathematically, it can be stated that if Δx is the uncertainty in the position of the object and Δp the uncertainty in its momentum, then the product of these two uncertainties must satisfy the relation:

$$\Delta p.\ \Delta x \geq \frac{h}{4\pi} \qquad (1.2)$$

Eq. 1.2 implies that if we make the measurement of the momentum of an object more precise, our knowledge of its position becomes correspondingly less precise and vice-versa.

[1] *A crystal is a natural grating with spacing just right for the wavelength associated with diffracting X-rays or electrons.*

Since $p = mv$, therefore, $\Delta p = m\Delta v$. The above relation, therefore, can also be written as

$$(m\Delta v)(\Delta x) \geq \frac{h}{4\pi}$$

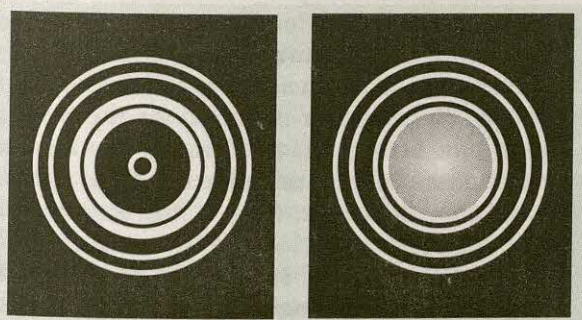
$$or\ \Delta v.\ \Delta x \geq \frac{h}{4\pi.m} \qquad (1.3)$$

which means that **position and velocity of an object cannot be simultaneously known with certainty**.

It must be understood that the **uncertainty principle applies to location and momentum along the same axis** i.e., if Δx is the uncertainty in position along x-axis, then Δp must also be the uncertainty in momentum along x-axis. Here it may be emphasised that this principle is not due to any limitation of the measuring instrument.

1.2.1 Significance of Uncertainty Principle

One of the important implications of the Heisenberg Uncertainty Principle is that **it rules out existence of definite paths or trajectories**. The trajectory of an object is determined by its location and velocity at various moments. If we know where a body is at a particular instant and if we also know its velocity and the forces acting on it at that instant, we can tell where the body would be sometime later. We, therefore, conclude that the position of an object and its velocity fix its trajectory. Since for a sub-atomic object such as an electron, it is not possible to simultaneously determine the position and velocity at any given instant to an arbitrary degree of precision, it is not possible to talk of the trajectory of an electron.



(a) (b)

Fig. 1.1 *(a) The X-ray diffraction pattern of aluminum foil. (b) The electron diffraction pattern of aluminum foil. The similarity of these two patterns shows that electrons can behave like X-rays and display wave properties.*

Werner Heisenberg
(1901-1976)
Werner Heisenberg (1901-1976) received his Ph.D. in physics from the University of Munich in 1923. He then spent a year working with Max Born at Göttingen and three years with Niels Bohr in Copenhagen. He was professor of physics at the University of Leipzig from 1927 to 1941. During World War II, Heisenberg was in charge of German research on the atomic bomb. After the war he was named director of the Max Planck Institute for Physics in Göttingen. He was also an accomplished mountain climber. Heisenberg was awarded the Nobel Prize in Physics, 1932.

The effect of Heisenberg Uncertainty Principle is, significant only for motion of microscopic objects and is negligible for that of macroscopic objects. This can be seen from the following examples.

If uncertainty principle is applied to an object of mass, say about a milligram (10^{-6} kg), then

$$\Delta v.\ \Delta x = \frac{h}{4\pi.m} = \frac{6.626\times10^{-34}\ \text{J s}}{4\times3.1416\times10^{-6}\,\text{kg}} \approx 10^{-28}\ \text{m}^2\text{s}^{-1}$$

The value of $\Delta v.\Delta x$ obtained is extremely small and therefore one may say that **in dealing with milligram-sized or heavier objects, uncertainties of such small dimensions are hardly of any real consequence**.

In the case of a microscopic object like an electron on the other hand, $\Delta v.\Delta x$ obtained is much larger and such uncertainties are of real consequence. For example, for an electron whose mass is 9.11×10^{-31} kg, according to Heisenberg uncertainty principle

$$\Delta v.\ \Delta x = \frac{h}{4\pi.\ m} = \frac{6.626\times10^{-34}\ \text{Js}}{4\times3.1416\times9.11\times10^{-31}\,\text{kg}}$$

$$\approx 10^{-4}\ \text{m}^2\text{s}^{-1}$$

It, therefore, means that if one tries to find the exact location of the electron, say to an uncertainty of only 10^{-8} m, then the uncertainty Δv in velocity would be $\dfrac{10^{-4}\ \text{m}^2\text{s}^{-1}}{10^{-8}\ \text{m}} \approx 10^{+4}\ \text{m s}^{-1}$, which is so large that the classical picture of electrons moving in Bohr's orbits (fixed) cannot hold good. **It, therefore, means that the precise statements of the position and momentum**

of electrons have, to be replaced by the statements of probability that the electron has a given position and momentum. This is what happens in the quantum mechanical model of atom.

Example 1.2
A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1Å. What is the uncertainty involved in the measurement of its velocity?
Mass of electron = 9.11×10^{-31} kg and
$h = 6.626\times10^{-34}$ J s.

Solution

$$\Delta x \times \Delta p = \frac{h}{4\pi} \quad \text{or} \quad \Delta x \times m\Delta v = \frac{h}{4\pi}$$

$$\Delta v = \frac{h}{4\pi \times \Delta x \times m}$$

$$\Delta v = \frac{6.626\times10^{-34}\,\text{J s}}{4\times3.14\times0.1\times10^{-10}\,\text{m}\times9.11\times10^{-31}\,\text{kg}}$$

$$= 0.579\times10^{7}\,\text{m s}^{-1} (1\,\text{J} = 1\,\text{kg m}^2\text{s}^{-2})$$

$$= 5.79\times10^{6}\,\text{m s}^{-1}$$

1.3 QUANTUM MECHANICS

On the basis of dual nature of matter and Heisenberg Uncertainty Principle, **Erwin Schrödinger**, an Austrian physicist, in 1926, developed a new branch of science called **quantum mechanics**, (also known as **wave mechanics**). **Schrödinger equation**, for a system such as an atom or a molecule whose energy does not change with time (time-independent), is written as

$$\hat{H}\Psi = E\Psi \qquad (1.4)$$

where $\hat{H}$ is the total energy operator[2] called Hamiltonian. Hamiltonian operator is the sum of kinetic energy operator ($\hat{T}$) and potential energy operator ($\hat{V}$) i.e., $\hat{H} = \hat{T} + \hat{V}$. The potential energy operator $\hat{V}$ for a system is normally equal to its expression for potential energy, V. Ψ (Greek psi, pronounced 'sigh') is the wave function of the system and E is the total energy of the system. Eq. (1.4) may therefore be written as $(\hat{T}+\hat{V})\psi = E\psi$. Writing Schrödinger equation for a system, therefore, means writing the explicit mathematical forms of $\hat{T}$ and $\hat{V}$ in the above equation. This equation is then solved to get E and ψ for the system.

The quantum mechanical study of any system consists of

1. Writing Schrödinger equation for the system.
2. Solving Schrödinger equation for the meaningful solutions of the wave functions and the corresponding energies. The meaningful solutions of ψ function must follow the conditions i.e., they have to be single valued, continuous and finite.
3. Calculation of all the observable properties of the system from ψ.

The quantum mechanical approach has gained wide acceptance as the results obtained are in excellent agreement with the experimental findings. In particular, the Schrödinger equation is very well suited to interpret the experimental information about the structure of atoms and molecules. A detailed presentation of the quantum mechanical approach is beyond the scope of this book and here we shall describe only a few **qualitative features of the electron behaviour in a hydrogen atom**.

1.4 QUANTUM MECHANICAL TREATMENT OF THE HYDROGEN ATOM

Hydrogen atom is the simplest chemical system consisting of one proton and one electron. Assuming that the electron moves at a distance r around the stationary nucleus, then the nucleus can be taken as the origin in a coordinate system. Schrödinger equation for the hydrogen atom can be written in terms of the cartesian coordinates (x, y, z) or in terms of the spherical polar coordinates (r, θ, φ) of the electron with respect to the nucleus. Since an atom has spherical symmetry, **it is more convenient to write Schrödinger equation in terms of polar coordinates**. The relationships between the two coordinate systems are shown in Fig. 1.2.

The coordinates x, y and z of the electron with respect to nucleus in terms of polar

[2] *In quantum mechanics, there is an 'operator' corresponding to every observable property. An 'operator' is like a mathematical command which acts on a mathematical function.*

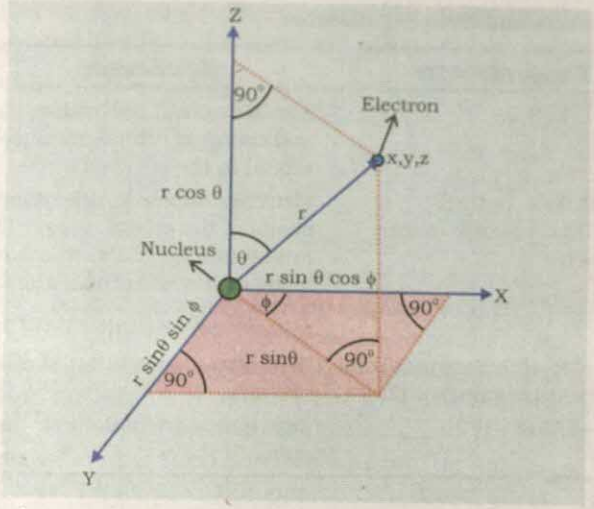


Fig. 1.2 *The relationship between cartesian (x,y,z) and polar coordinates (r, θ, φ).*

coordinates are given by:

$$x = r \sin\theta \cos\varphi$$
$$y = r \sin\theta \sin\varphi \qquad (1.5)$$
$$z = r \cos\theta$$
$$x^2 + y^2 + z^2 = r^2$$

When Schrödinger equation in polar coordinates is solved for the hydrogen atom, it gives the possible energy states and the corresponding wave function [ψ (r, θ, φ)] (called **atomic orbitals** or **hydrogenic orbitals**, which are in fact the mathematical functions of the coordinates of the electron associated with each energy state). It can be shown that an atomic orbital is the product of two factors: (i) the radial part, dependent on r and (ii) the angular part, dependent on θ and φ. The quantized electronic states of the hydrogen atom are given by

$$E_n = \frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} \text{ (in SI units)} \qquad (1.6)$$

where m_e^* is the mass of electron in kg, e its charge in C, h the Planck constant and n the principal quantum number. ε_0 is the permittivity of free space, and is a measure of how easy it is for electromagnetic radiation to pass through it. **It is interesting to note that the electronic energy of the hydrogen atom depends only on *n* and is independent of *l* and *m*.**

The above quantised energy states and corresponding wave functions which are characterised by a set of three quantum numbers (principal quantum number n, azimuthal quantum number l and magnetic quantum number m_l) arise as a natural consequence in the solution of the Schrödinger equation. The restrictions on the values of these three quantum numbers also come naturally from this solution. The quantum mechanical solution of the hydrogen atom successfully predicts all aspects of the hydrogen atom spectrum and other phenomena that could not be explained by the Bohr model.

The Schrodinger equation cannot be solved exactly for a multi-electron atom. However, solutions of reasonable accuracy can be obtained using approximate methods. The total wave function for a multi-electron atom can be constructed from atomic orbitals having different energies. These atomic orbitals are the function of coordinates of a single electron and their angular part has the same form as for hydrogen atom depending upon l and m_l values. However, their radial part is different and also takes into account the mutual repulsion between the electrons and depends on n, l and charge Z, on the nucleus. According to the quantum mechanical model of atom, these **atomic orbitals form the basis of electronic structure of atoms**. In a multi-electron atom the electrons are filled in various orbitals in order of increasing energy according to certain rules which we shall take up in section 1.6.

1.4.1 Quantum Numbers

Each atomic orbital in an atom is designated by a set of three quantum numbers viz. principal quantum number (n), azimuthal quantum number (l) and magnetic quantum number (m_l). **These quantum numbers also help to designate the electron present in an orbital.** Further since an orbital can contain a maximum of two electrons with opposite spins, an additional quantum number known as the magnetic spin quantum number (m_s) is required to specify the spin of the electron. This quantum number, unlike

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* *In actual calculations μ (reduced mass) is used in place of* m_e $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_n}$

where m_n *is the mass of the nucleus. The mass of the nucleus is much larger than the mass of the electron and therefore except for the most precise work, reduced mass can be taken to be equal to* m_e.

Table 1.1 Quantum Numbers and their Significance

Quantum Number	Symbol	Restrictions	Range of values	Significance
Principal quantum number	n	Positive integers	1, 2, 3	identifies shell, determines size and energy of orbital, number of orbital in the n^{th} shell = n^2
Azimuthal quantum number or Angular momentum quantum number	l	Positive integers less than n	0, 1, 2 .... $(n-1)$ Total possible values = n	identifies subshell; determines shape of the orbital, energy of orbital in a multi-electron atom along with n and orbital angular momentum i.e. $\sqrt{l(l+1)}\,h/2\pi$
Magnetic quantum number	m_l	Integers between $-l$ and $+l$	$-l$ to $+l$ including 0 Total possible values = $(2l+1)$	determines orientation of the orbital
Magnetic spin quantum number	m_s	Half integers +1/2 or −1/2	+1/2 or −1/2	determines orientation of the spin

the above three quantum numbers is not derived from the solution of the Schrödinger equation for hydrogen atom. **The state of an electron in an atom is specified by the four quantum numbers namely n, l, m_l and m_s.**

You have already learnt (Class XI) about these quantum numbers and the information they provide. A brief review of this is given in Table 1.1.

Magenetic Spin Quantum Number

An electron, besides charge and mass, has also spin angular momentum commonly called **spin**. The spin angular momentum of the electron is constant and cannot be changed. The magnitude of the spin angular momentum of an electron is

$\sqrt{s(s+1)}\,\frac{h}{2\pi}$, with spin quantum number, $s = 1/2$

i.e., $\frac{\sqrt{3}}{4\pi}h$. **Spin angular momentum, is a vector quantity and can have only two orientations relative to a chosen axis** (Fig. 1.3). They are distinguished by the magenetic quantum number m_s which can take the values + ½ and − ½ . These two spin states of the electron are normally represented by two arrows ↑(spin-up) and ↓ (spin-down). The components of the spin angular momentum vector around the chosen axis are limited to $\pm\frac{1}{2}\frac{h}{2\pi}$. Classically, we can picture the two spin states as the rotation of an electron on its axis either clockwise or counter-clockwise. However, spin is a purely quantum mechanical property and differs from its classical namesake.

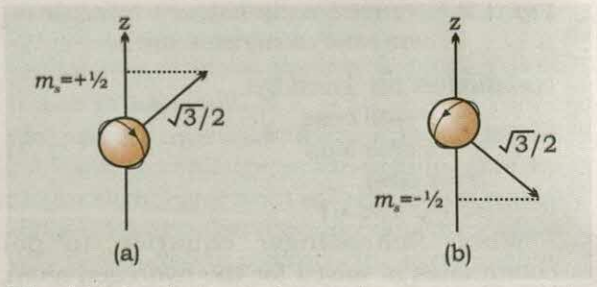


Fig. 1.3 *An electron spin angular momentum vector of length $\sqrt{3}/2$ units (one unit $= h/2\pi$) can take only two orientations with respect to a specified axis.*

1.5 ATOMIC ORBITALS AND THEIR PICTORIAL REPRESENTATIONS

An atomic orbital is a one electron wave function $\Psi(r, \theta, \varphi)$ obtained from the solution of the Schrödinger equation for the hydrogen atom. It is a mathematical function of the three coordinates of the electron (r, θ, φ) and can be factorised into three separate parts each of which is a function of only one coordinate:

$$\Psi(r, \theta, \varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi)$$

where **R (r) is the radial function** which gives the dependence of orbital upon distance r of the electron from the nucleus and **$\Theta(\theta)$ and $\Phi(\varphi)$ are the angular functions** giving the angular dependence of orbital on θ and φ respectively. Further, the radial function depends upon the quantum numbers n and l, whereas the angular part depends upon quantum numbers l and m_l

and is independent of n. The total wave function Ψ may, therefore, be more explicitly written as

$$\Psi(r, \theta, \varphi) = \underbrace{R_{n,l}(r)}_{\text{Radial part}} \underbrace{\Theta_{l,m_l}(\theta)\, \Phi_{m_l}(\varphi)}_{\text{Angular part}}$$

The orbital wave function Ψ has no physical significance. It is the square of the absolute value of the orbital wave function $|\Psi|^2$ which has a physical significance – it measures the electron probability density at a point in an atom. It would, therefore, be interesting to know how Ψ and $|\Psi|^2$ vary as a function of the three coordinates r, θ and φ for different orbitals. Such representation of the variations of Ψ or $|\Psi|^2$ in space would however need a four dimensional graph–three dimensions for the coordinates and the fourth for Ψ or $|\Psi|^2$. It is not possible to show such variation in a single diagram since we can draw only two-dimensional diagrams on paper. We can get around this difficulty by drawing separate diagrams for: (i) variation of radial function and (ii) angular function. These plots are discussed below.

1.5.1 Plots of the Radial Wave Function $R_{n,l}(r)$

The plots of the radial wave function $R_{n,l}(r)$, radial probability density $R^2_{n,l}(r)$ and radial probability function $4\pi r^2 R^2_{n,l}(r)$ for *1s* ($n = 1$, $l = 0$), *2s* ($n = 2$, $l = 0$) and *2p* ($n = 2$, $l = 1$) atomic orbitals as a function of the distance r from the nucleus are shown in Fig. 1.4(a-c). Let us briefly discuss each of these plots separately.

A. Radial wave function [$R_{n,l}(r)$] [Fig. 1.4(a)]

In all cases $R_{n,l}(r)$ approaches zero as r approaches infinity. One finds that in the plot of 2*s* radial function, the value of the radial function passes through zero and changes from positive to negative. The region where $R_{n,l}(r)$ is zero is called node. In general, it has been found that *ns*-orbitals have $(n-1)$ nodes, *np*-orbitals have $(n-2)$ nodes etc.

The importance of these plots lies in the fact that they give information about how the radial wave function changes with distance r and about the presence of nodes, where the change of sign of $R_{n,l}(r)$ occurs.

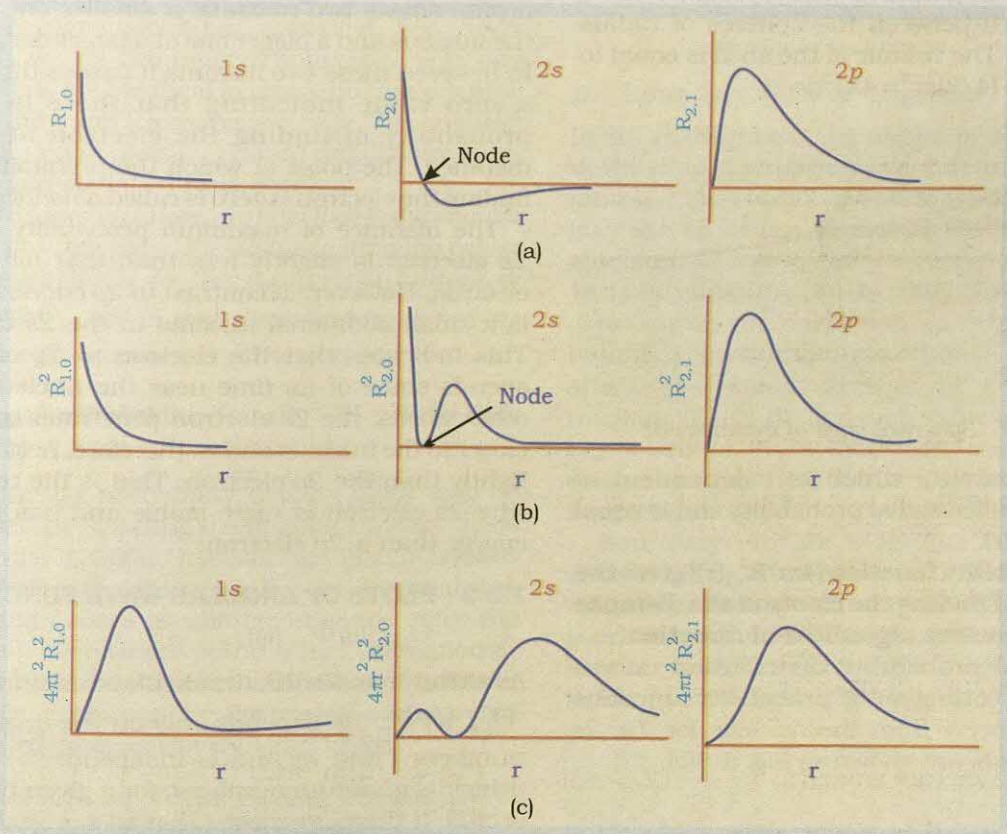


Fig. 1.4 *The plots of (a) the radial wave function $R_{n,l}(r)$ (b) the radial probability density $R^2_{n,l}(r)$ and (c) the radial density function $4\pi r^2 R^2_{n,l}(r)$ as a function of distance r of the electron from the nucleus for 1s, 2s and 2p orbitals. The plots are not drawn to scale.*

B. Radial probability density $[R^2_{n,l}(r)]$ [Fig. 1.4 (b)]

The square of the radial wave function $R^2_{n,l}(r)$ for an orbital gives the radial density. The radial density gives the probability density of finding the electron at a point along a particular radius line. To get such a variation, the simplest procedure is to plot $R^2_{n,l}(r)$ against r [Fig. 1.4(b)]. These plots give useful information about probability density or relative electron density at a point as a function of radius. It may be noted that while for s-orbitals the maximum electron density is at the nucleus, all other orbitals have zero electron density at the nucleus.

C. Radial probability functions $4\pi r^2 R^2_{n,l}(r)$ [Fig. 1.4(c)]

The radial density $R^2_{n,l}(r)$ for an orbital, as discussed above, gives the probability density of finding the electron at a point at a distance r from the nucleus. Since the atoms have spherical symmetry, it is more useful to discuss the probability of finding the electron in a spherical shell between the spheres of radius (r + dr) and r. The volume of the shell is equal to $(4/3)\pi(r+dr)^3 - (4/3)\pi r^3 = 4\pi r^2 dr$.

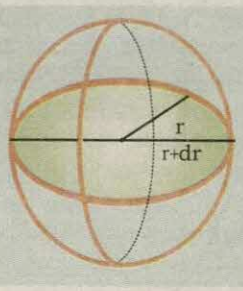


Fig. 1.5 *Spherical shell of thickness dr.*

This probability which is independent of direction is called radial probability and is equal to $4\pi r^2 dr\, R^2_{n,l}(r)$.

Radial probability function $[4\pi r^2 R^2_{n,l}(r)]$ gives the probability of finding the electron at a distance r from the nucleus regardless of direction.

The radial probability distribution curves obtained by plotting radial probability functions versus distance r from the nucleus for *1s*, *2s* and *2p* orbitals are shown in Fig. 1.4(c).

1s orbital

The radial probability function for the 1*s* orbital initially increases with increase in distance from the nucleus. It reaches a maximum at a distance very close to the nucleus and then decreases. **The maximum in the curve corresponds to the distance at which the probability of finding the electron is maximum**. This distance is called the ***radius of maximum probability*** and for hydrogen atom has a value of 52.9 pm.

It may be noted that while Bohr's model restricts the electron to a definite orbit at a fixed distance from the nucleus, the quantum mechanical model gives merely the maximum probability of finding the electron at 52.9 pm distance from the nucleus. In the case of hydrogen atom, for instance, according to Bohr model, the electron always stays at a distance of 52.9 pm from the nucleus. According to the quantum mechanical model, however, *the electron in the hydrogen atom can be at any distance but the most probable distance for finding the electron is 52.9 pm.*

2s and 2p orbitals

The radial probability function curve for 2*s* orbital shows two maxima, a smaller one near the nucleus and a bigger one at a larger distance. In between these two maxima it passes through a zero value indicating that there is zero probability of finding the electron at that distance. The point at which the probability of finding the electron is zero is called a *nodal point.*

The distance of maximum probability for a *2p* electron is slightly less than that for a *2s* electron. However, in contrast to *2p* curve, there is a small additional maxima in the *2s* curve. This indicates that the electron in *2s* orbital spends some of its time near the nucleus. In other words, the *2s* electron penetrates a little closer to the nucleus and is, therefore, held more tightly than the *2p* electron. That is the reason why *2s* electron is more stable and has lower energy than a *2p* electron.

1.5.2 PLOTS OF ANGULAR WAVE FUNCTION $\Theta_{l,m_l}(\theta)\,\Phi_{m_l}(\varphi)$

As already mentioned, the angular wave function '$\Theta_{l,m_l}(\theta)\,\Phi_{m_l}(\varphi)$' depends only on the quantum numbers l and m_l and is independent of the principal quantum number n for a given type of orbital. It therefore means that all *s* orbitals will have same angular wave function. The plots of the angular wave function '$\Theta_{l,m_l}(\theta)\,\Phi_{m_l}(\varphi)$' and

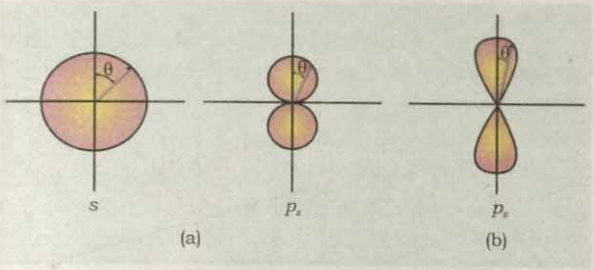


Fig. 1.6 *(a) Angular part of the wave function for hydrogen-like s orbitals and p_z orbital (b) Angular probability function for p_z orbital. Only two dimensions of the three-dimensional function have been shown.*

angular probability density $|\Theta_{l,m_l}(\theta)\Phi_{m_l}(\varphi)|^2$ for *s* and p_z orbitals are shown in [Fig. 1.6(a, b)]. Let us discuss both these plots separately.

A. Angular Wave Function, $\Theta_{l,m_l}(\theta)\Phi_{m_l}(\varphi)$ [Fig. 1.6(a)]

For an *s*- orbital, the angular part is independent of angle and is, therefore, of constant value. Hence this graph is circular or, more properly, in three dimensions i.e., spherical. For the p_z orbital, we get two tangent spheres. The p_x and p_y orbitals are identical in shape but are oriented along the *x* and *y* axes respectively. The angular, wave function plots for *d* and *f* orbitals are four-lobed and six-lobed respectively.

It is necessary to keep in mind that in the angular wave function plots, the distance from the center is proportional to the numerical values of '$\Theta_{l,m_l}(\theta)\Phi_{m_l}(\varphi)$' in that direction and is not the distance from the center of the nucleus.

B. Angular Probability Density $|\Theta_{l,m_l}(\theta)\Phi_{m_l}(\varphi)|^2$ [Fig. 1.6(b)]

The angular probability density plots can be obtained by squaring the angular function plots shown in Fig. 1.6(a). On squaring, different orbitals change in different ways. For an s orbital, the squaring causes no change in shape since the function everywhere is the same; thus another sphere is obtained. For both *p* and *d* orbitals, however, on squaring the plot tends to become more elongated as shown for p_z in Fig. 1.6(b).

1.5.3 Plots of Total Probability Density: Shapes of Atomic Orbitals

The problems associated with the representations of the variations of $|\Psi|^2$ in space have been circumvented by the following two approaches:

(a) Charge cloud diagrams
(b) Boundary surface diagrams

A. Charge cloud diagrams

In this approach, the probability density $|\Psi|^2$ is shown as a collection of dots such that the density of dots in any region represents the electron probability density in that region. Fig. 1.7 shows such plots for some orbitals. These give some idea about the shapes of the orbitals.

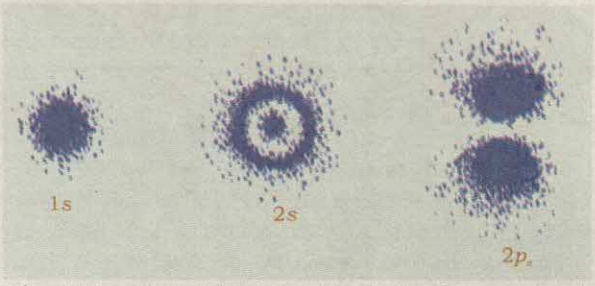


Fig. 1.7 *Probability density plots of some atomic orbitals. The density of the dots represents the probability density of finding the electron in that region.*

B. Boundary surface diagrams

In these diagrams, the **shape of an orbital is defined as a surface of constant probability density that encloses some large fraction (say 90 %) of the probability of finding the electron**. The probability density is $|\Psi|^2$. When $|\Psi|^2$ is constant, so is $|\Psi|$. Hence $|\Psi|$ is constant on the surface of an orbital. Such a boundary surface for an s orbital ($l = 0$) has the shape of a spherical shell centered on the nucleus, (Fig. 1.8). For each value of n, there is one s orbital. As *n* increases, there are $(n-1)$ concentric spherical shells like the successive layers in an onion.

Boundary surface diagrams for the three *2p* orbitals (l=1) are shown in Fig. 1.9. In these diagrams, the nucleus is at the origin. Each *p*-orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The size, shape and

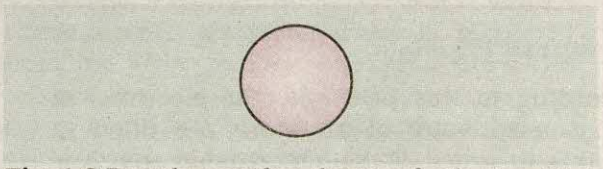


Fig. 1.8 *Boundary surface diagram for the 1s orbital.*

energy of the three orbitals are identical. They differ, however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z axis, they are given the designations $2p_x$, $2p_y$, and $2p_z$. Like s orbitals, p orbitals increase in size with increase in the principal quantum number and hence $4p > 3p > 2p$.

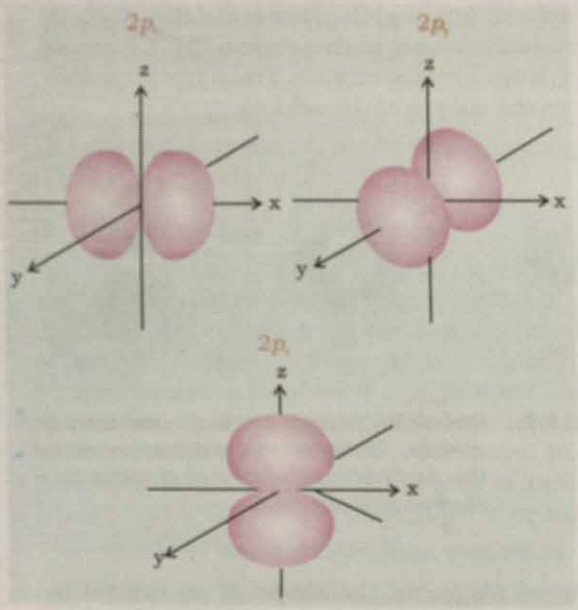


Fig. 1.9 *Boundary surface diagrams of the three 2p orbitals.*

Boundary surface diagrams of the d orbitals ($l = 2$) are shown in Fig. 1.10. There are five d orbitals which are designated as d_{xy} d_{yz} d_{xz} $d_{x^2-y^2}$ and d_{z^2}. The shape of $3d_{z^2}$ orbital is different from that of others but all five $3d$ orbitals are equivalent in energy. The d orbitals for which n is greater than 3 ($4d$, $5d$, ...) have similar shapes.

1.6 ELECTRONIC CONFIGURATION OF ELEMENTS

The distribution of electrons of an atom in its various orbitals is called its electronic configuration. You have already studied in Class XI the basic rules which govern the filling of atomic orbitals in atoms. Here we shall briefly review these rules.

A. Aufbau Principle

According to this principle, the electrons in the ground state of an atom are filled in orbitals in order of their increasing energies.

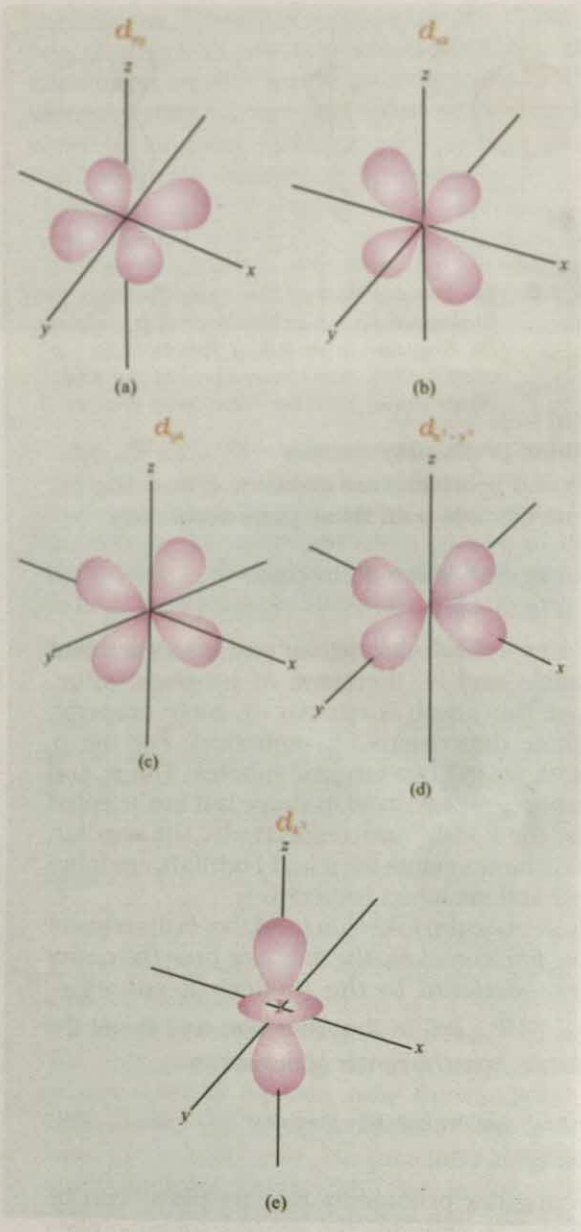


Fig. 1.10 *Boundary surface diagrams of the five 3d orbitals.*

The order of increase of energy of orbitals can be calculated from the $(n + l)$ rule explained below:

1. The lower the value of $(n + l)$ for an orbital, the lower is its energy. This means that between $3d$ and $4s$, the $4s$ $(n + l = 4 + 0 = 4)$ will fill before $3d$ $(n + l = 3 + 2 = 5)$.
2. If two orbitals have the same $(n+l)$, the one with lower n will be filled first. Thus, between

Stability of Completely Filled and Half Filled Subshells

The ground state electronic configuration of the atom of an element always corresponds to the state of the lowest total electronic energy. The electronic configurations of most of the atoms follow the basic rules given in Section 1.6. However, in certain elements such as Cu, or Cr, where the two subshells (*4s* and *3d*) differ slightly in their energies, an electron shifts from a subshell of lower energy (*4s*) to a subshell of higher energy (*3d*), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half filled. The valence electron configurations of Cr and Cu, therefore, are $4s^1 3d^5$ and $4s^1 3d^{10}$ respectively and not $4s^2 3d^4$ and $4s^2 3d^9$. It has been found that there is extra stability associated with these electronic configurations. This stabilization is due to the following two factors :

1. **Symmetrical distribution of electrons**: It is well known that symmetry leads to stability. The completely filled or half filled subshells have symmetrical distribution of electrons in them and are therefore more stable. Electrons in the same subshell (here *3d*) have equal energy but different spatial distribution. Consequently, their shielding of one-another is relatively small and the electrons are more strongly attracted by the nucleus.
2. **Exchange Energy**: This stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or completely filled (Fig. 1.11). As a result the exchange energy is maximum and so is the stability.

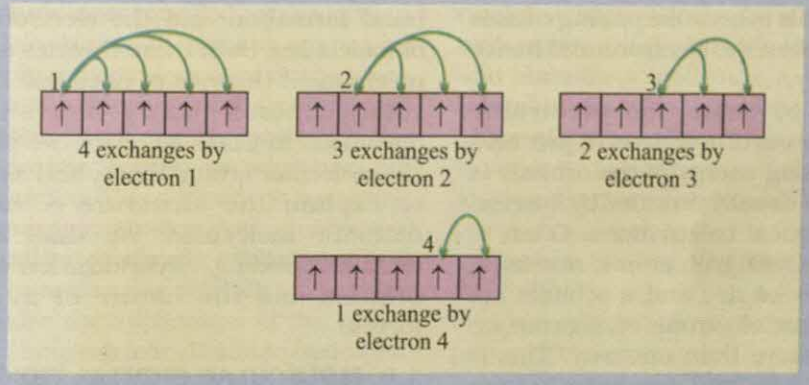


Fig. 1.11 *Possible exchanges for a d^5 configuration.*

2p ($n + l = 2 + 1 = 3$) and 3s ($n + l = 3 + 0 = 3$), *2p* will fill before 3s.

The order in which the energies of the orbitals increase and hence the order in which the orbitals are filled is as follows:

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p

B. Pauli Exclusion Principle

No two electrons in an atom can have the same set of four quantum numbers.

C. Hund's Rule of Maximum Multiplicity

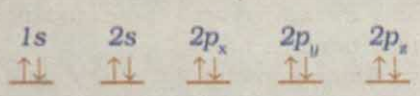
Pairing of electrons in the orbitals belonging to the same subshell (*p*, *d* or *f*) does not take place until each orbital belonging to that subshell has got one electron each, i.e., is singly occupied.

Using the above rules, the electronic configurations of different elements can be written very easily.

1.6.1 Representation of the Electronic Configurations

The electronic configuration of the atom of an element is written by filling of atomic orbitals in increasing order of their energies. Thus, the electronic configuration of neon, for example, is written as $1s^2 2s^2 2p^6$. The only drawback of writing electronic configuration by this method,

known as *orbital notation method*, is that one can get no idea about the spins of individual electrons from the notations. In order to get a pictorial view, the orbitals may be represented by lines or boxes and the electrons by arrows. The spins of the electrons being represented by the direction of these arrows. This method of writing electronic configuration is called *orbital diagram method*. Thus, the electronic configuration of neon can be shown as

i) 

or ii)

In the same manner, the electronic configurations of all the elements can be represented. In the case of orbitals of a subshell, the filling of the orbitals takes place in such a manner that the total spin angular momentum is maximum, i.e., these orbitals are initially singly occupied and then pairing of electron spins takes place. This is because pairing causes more repulsion between the electrons and hence increases the energy.

It is possible to write the electronic configuration of an atom of any element provided the order of increasing energy of the orbitals is known. This order is usually provided by spectral data or from theoretical calculations. Often in the case of elements with high atomic numbers, the relative energies of *d*, *f* and *s* orbitals are similar and hence their electronic configurations can be written in more than one way. This is true of the transition and inner-transition elements (Unit 9).

1.7 CHEMICAL BONDING

A molecule is formed from the combination of two or more than two atoms of the same or different elements and has characteristic properties of its own. A molecule is formed because it has a lower energy (and hence is stable) as compared to the constituent atoms existing separately. It is convenient to think that atoms in a molecule are linked by chemical bonds. **A chemical bond may be defined as the force that holds the atoms together within a molecule.** There are many types of chemical bonds such as covalent bond, ionic bond, metallic bond, hydrogen bond etc. depending upon the nature of the force holding the atoms together.

Robert S. Mulliken

Robert S. Mulliken (b. 1896) received his Ph.D. in Physical Chemistry from the University of Chicago in 1921, and then did Post Doctoral study at Chicago, Harvard and Göttingen. He returned to the University of Chicago in 1928 with a joint appointment in the departments of physics and chemistry. Mulliken was awarded the Nobel Prize for Chemistry in 1966.

In 1916, G.N. Lewis put forward his electronic theory to explain the formation of ionic bond and covalent bond. You have already learnt about this theory and its limitations in Class XI.

Two theories of chemical bonding, namely, **valence bond theory** and **molecular orbital theory** have been proposed to describe covalent bond formation and the electronic structure of molecules. Both these theories are quantum-mechanical theories of chemical bonding. The valence bond theory has already been discussed in Class XI. Here we shall describe the molecular orbital theory and its applications to explain the structure of homonuclear diatomic molecules. We shall also discuss metallic bonding, hybridization of *s*, *p* and *d* orbitals and the nature of intermolecular forces.

1.8 MOLECULAR ORBITAL THEORY

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features of this theory are:

(i) Just as electrons of atoms are present in various atomic orbitals, electrons of a molecule are present in various molecular orbitals.

(ii) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.

(iii) While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. **Thus an atomic orbital is monocentric while a molecular orbital is polycentric.**

(iv) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called **bonding molecular orbital** and **antibonding molecular orbital** are formed.

(v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

(vi) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.

(vii) The molecular orbitals like atomic orbitals are filled in accordance with the Aufbau principle obeying the Pauli principle and the Hund's rule.

1.8.1 Formation of Molecular Orbitals: Linear Combination of Atomic Orbitals (LCAO)

In principle, Schrödinger equation can be written for any molecule. However, since it cannot be solved exactly for any system containing more than one electron, molecular orbitals which are one electron wave functions for molecules are difficult to obtain directly from the solution of the Schrödinger equation. This difficulty is overcome by resorting to an approximation method called the **linear combination of atomic orbitals (LCAO) method to form molecular orbitals**.

Let us consider the application of the LCAO method to the homonuclear diatomic hydrogen molecule. The two hydrogen atoms in the H_2 molecule, for the sake of convenience may be labelled as A and B. Each hydrogen atom in ground state has one electron in the 1s orbital. These atomic orbitals may be represented by the wave functions ψ_A and ψ_B. Mathematically the formation of molecular orbitals is described by the linear combination (addition or subtraction of the wave functions of the individual atomic orbitals) of ψ_A and ψ_B as shown below.

$$\psi_{MO} = \psi_A \pm \psi_B$$

Therefore, two molecular orbitals σ and σ^* are formed as

$$\sigma = \psi_A + \psi_B$$
$$\sigma^* = \psi_A - \psi_B$$

The molecular orbital σ formed by the addition of atomic orbitals is called the **bonding molecular orbital** and the molecular orbital σ^* formed by the subtraction of atomic orbitals is called **antibonding molecular orbital** (Fig. 1.12).

Qualitatively, the formation of molecular orbitals can be understood in terms of the constructive or destructive interference of the electron waves of the combining atoms. In the formation of bonding molecular orbital, the two electron waves of the bonding atoms reinforce each other (constructive interference) while in the formation of antibonding molecular orbital, these electron waves cancel each other (destructive interference). The result is that in a bonding molecular orbital most of the electron density is located between the nuclei of the bonded atoms and hence the repulsion between the nuclei is very low while in an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei, as a matter of fact there is a ***nodal plane*** **(i.e., plane in which the electron density is zero)** between the nuclei and hence the repulsion between the nuclei is high. Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilize a molecule. A bonding molecular orbital is, therefore, always of lower energy than either of the atomic orbitals that have combined to form it. In contrast, electrons placed in the antibonding molecular orbital destabilize the

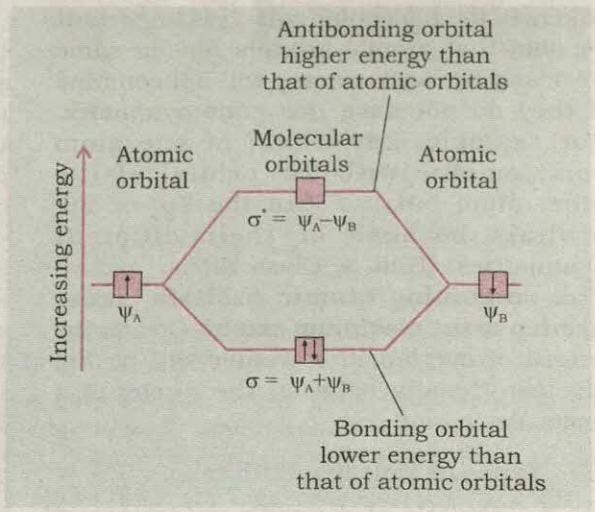


Fig. 1.12 *Formation of bonding (σ) and antibonding (σ^*) molecular orbitals by the linear combination of atomic orbitals Ψ_A and Ψ_B centered on two atoms A and B respectively.*

molecule. The attraction between the electrons and the nuclei is less than the mutual repulsion of electrons in this orbital and this produces a net increase in energy. Consequently, the electrons placed in this molecular orbital lead to a destabilization of the molecule and that is why this orbital is said to be antibonding.

It needs to be pointed out that the **energy of the antibonding orbital is raised above the energy of the parent atomic orbitals that have combined and the energy of the bonding orbital has been lowered than the parent orbitals. The total energy of two molecular orbitals however remains the same as that of the two orginal atomic orbitals.**

1.8.2 Conditions for the Combination of Atomic Orbitals

The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied:

1. **The combining atomic orbitals must have the same or nearly the same energy.** This means that 1s orbital can combine with another 1s orbital but not with 2s orbital because the energy of 2s orbital is appreciably higher than that of 1s orbital. This is not true if the atoms are very different.
2. **The combining atomic orbitals must have the same symmetry about the molecular axis.** By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example, $2p_z$ orbital of one atom can combine with $2p_z$ orbital of the other atom but not with the $2p_x$ or $2p_y$ orbitals because of their different symmetries. (Unit 6, Class XI)
3. **The combining atomic orbitals must overlap to the maximum extent.** Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

1.8.3 Types of Molecular Orbitals

Molecular orbitals of diatomic molecules are designated as σ (sigma), π (pi), δ (delta), etc.

In this nomenclature, the **sigma (σ) molecular orbitals are symmetrical around the bond-axis while pi (π) molecular orbitals are not symmetrical.** For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbital's are of the σ type and are designated as $\sigma 1s$ and $\sigma^* 1s$ [Fig. 1.13(a)]. **If internuclear axis is taken to be in the z-direction, it can be seen that a linear combination of $2p_z$- orbitals of two atoms also produces two sigma molecular orbitals designated as $\sigma 2p_z$ and $\sigma^* 2p_z$.** [Fig. 1.13(b)]

Molecular orbitals obtained from $2p_x$ and $2p_y$ orbitals are not symmetrical around the bond axis because of the presence of positive lobes above and negative lobes below the molecular plane. Such molecular orbitals, are labelled as π and π* [Fig. 1.13(c)]. A π bonding MO has larger electron density above and below the inter-nuclear axis. The π* antibonding MO has a node between the nuclei.

1.8.4 Energy Level Diagram for Molecular Orbitals

We have seen that 1s atomic orbitals on two atoms form two molecular orbitals designated as $\sigma 1s$ and $\sigma^* 1s$. In the same manner, the 2s and 2p atomic orbitals (eight atomic orbitals on two atoms) give rise to the following eight molecular orbitals:

Antibonding MOs $\sigma^* 2s$ $\sigma^* 2p_z$ $\pi^* 2p_x$ $\pi^* 2p_y$

Bonding MOs $\sigma 2s$ $\sigma 2p_z$ $\pi 2p_x$ $\pi 2p_y$

The energy levels of these molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below :

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

However, this sequence of energy levels of molecular orbitals is not correct for the remaining molecules Li_2, Be_2, B_2, C_2, N_2. For instance, it has been observed experimentally that for molecules such as B_2, C_2, N_2 etc. the increasing order of energies of various molecular orbitals is

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

The important characteristic feature of this order is that the **energy of $\sigma 2p_z$ molecular orbital is higher than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.**

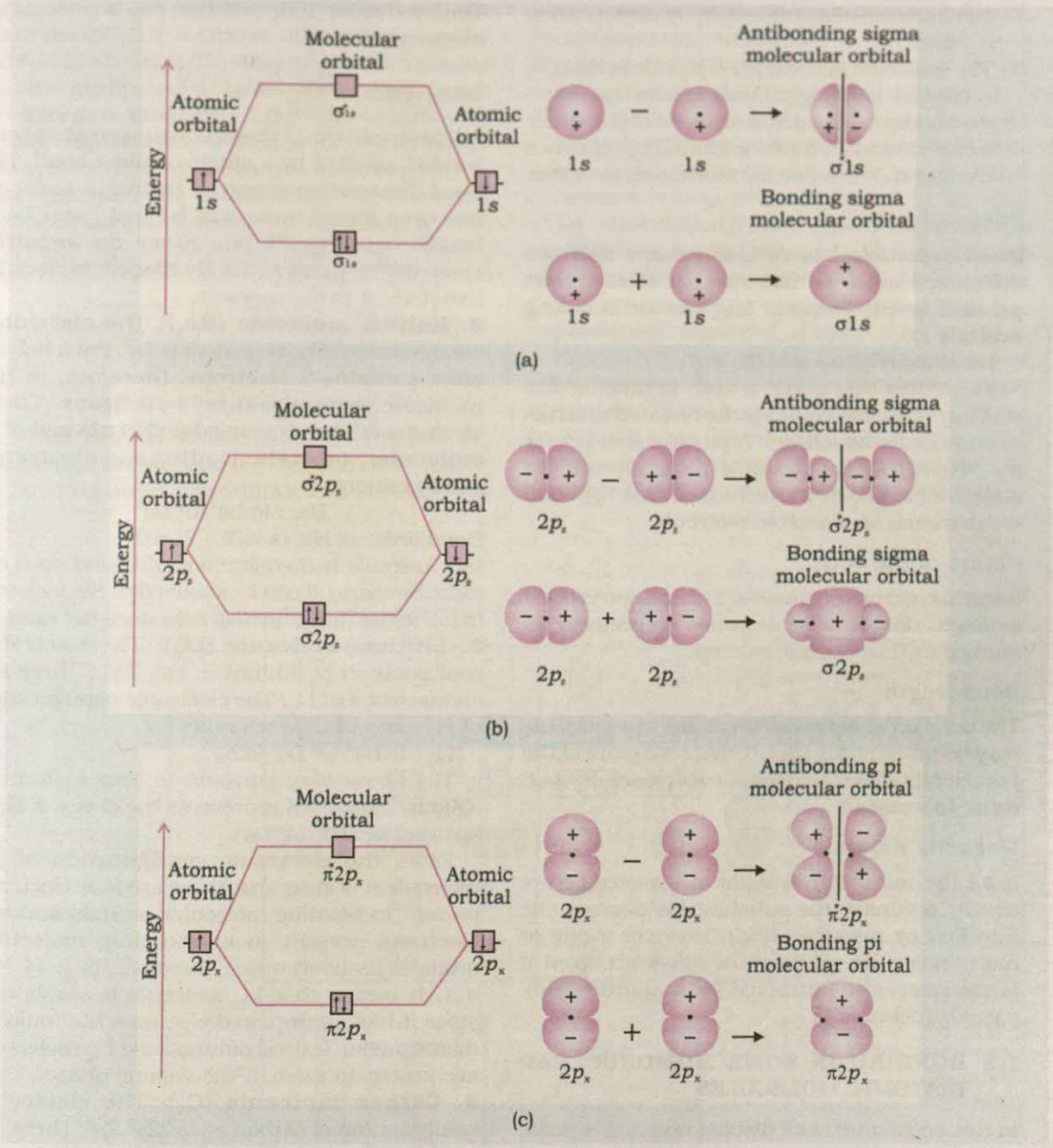


Fig. 1.13 *Contours and energies of bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b) $2p_z$ atomic orbitals and (c) $2p_x$ atomic orbitals.*

1.8.5 Electronic Configuration and Molecular Behaviour

The distribution of electrons among various molecular orbitals is called the **electronic configuration of the molecule**. From the electronic configuration of the molecule, it is possible to get important information about the molecule as discussed below.

Stability of Molecules: If N_b is the number of electrons occupying bonding orbitals and N_a the number occupying the antibonding orbitals, then

(i) The molecule is stable if N_b is greater than N_a, and

(ii) The molecule is unstable if N_b is less than N_a

In (i) more bonding orbitals are occupied and so the bonding influence is stronger and a stable molecule results. In (ii) the antibonding influence is stronger and therefore the molecule is unstable.

Bond order

Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals i.e.,

Bond order (b.o.) = ½ (N_b–N_a)

The rules discussed above regarding the stability of the molecule can be restated in terms of bond order as follows: A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative (i.e., $N_b < N_a$) or zero (i.e., $N_b = N_a$) bond order means an unstable molecule.

Nature of the bond

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively as studied in the classical concept.

Bond-length

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

Magnetic nature

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field). However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O_2 molecule.

1.9 BONDING IN SOME HOMONUCLEAR DIATOMIC MOLECULES

In this section we shall discuss bonding in some homonuclear diatomic molecules.

1. Hydrogen molecule (H_2): It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in 1s orbital. Therefore, in all there are two electrons in hydrogen molecule which are present in $\sigma 1s$ molecular orbital. So electronic configuration of hydrogen molecule is

$$H_2 : (\sigma 1s)^2$$

The bond order of H_2 molecule can be calculated as given below:

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

This means that the two hydrogen atoms are bonded together by a single covalent bond. The bond dissociation energy of hydrogen molecule has been found to be 438 kJ mol^{-1} and bond length equal to 74 pm. Since no unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

2. Helium molecule (He_2): The electronic configuration of helium atom is $1s^2$. Each helium atom contains 2 electrons, therefore, in He_2 molecule there would be 4 electrons. These electrons will be accommodated in $\sigma 1s$ and $\sigma^* 1s$ molecular orbitals leading to electronic configuration:

$$He_2 : (\sigma 1s)^2 (\sigma^* 1s)^2$$

Bond order of He_2 is ½(2 – 2) = 0

He_2 molecule is therefore unstable and does not exist. Similarly, it can be shown that Be_2 molecule $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$ also does not exist.

3. Lithium molecule (Li_2): The electronic configuration of lithium is $1s^2$, $2s^1$. There are six electrons in Li_2. The electronic configuration of Li_2 molecule, therefore, is

$$Li_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$$

The above configuration is also written as $KK(\sigma 2s)^2$ where KK represents the closed K shell structure $(\sigma 1s)^2 (\sigma^* 1s)^2$.

From the electronic configuration of Li_2 molecule it is clear that there are four electrons present in bonding molecular orbitals and two electrons present in antibonding molecular orbitals. Its bond order, therefore, is ½ (4 – 2) = 1. It means that Li_2 molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic Li_2 molecules are known to exist in the vapour phase.

4. Carbon molecule (C_2): The electronic configuration of carbon is $1s^2\ 2s^2\ 2p^2$. There are twelve electrons in C_2. The electronic configuration of C_2 molecule, therefore, is

$$C_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$$

or $$KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$$

The bond order of C_2 is ½ (8 – 4) = 2 and C_2 should be diamagnetic. Diamagnetic C_2 molecules have indeed been detected in vapour phase. It is important to note that double bond

in C_2 consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals. In most of the other molecules a double bond is made up of a sigma bond and a pi bond.

5. Oxygen molecule (O_2): The electronic configuration of oxygen atom is $1s^2\ 2s^2\ 2p^4$. Each oxygen atom has 8 electrons, hence, in O_2 molecule there are 16 electrons. The electronic configuration of O_2 molecule, therefore, is

$$O_2: \quad (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2$$

$$(\pi\, 2p_x^{\,2} \equiv \pi\, 2p_y^{\,2})\ (\pi^* 2p_x^{\,1} \equiv \pi^* 2p_y^{\,1}) \quad \text{or}$$

$$O_2: \quad \left[\begin{array}{c} KK\,(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2 \\ (\pi 2p_x^2 \equiv \pi 2p_y^2)\,(\pi^* 2p_x^1 \equiv \pi^* 2p_y^1) \end{array}\right]$$

From the electronic configuration of O_2 molecule it is clear that ten electrons are present in bonding molecular orbitals and six electrons are present in antibonding molecular orbitals. Its bond order, therefore, is

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[10-6] = 2$$

So in oxygen molecule, atoms are held by a double bond. Moreover, it may be noted that it contains two unpaired electrons in $\pi^* 2p_x$ and $\pi^* 2p_y$ molecular orbitals, therefore, **O_2 molecule should be paramagnetic, a prediction that corresponds to experimental observation**. In this way, the theory successfully explains the paramagnetic nature of oxygen.

Similarly, the electronic configurations of other homonuclear diatomic molecules of the second row of the periodic table can be written. In Fig.1.14 are given the molecular orbital occupancy and molecular properties for B_2 through Ne_2. The sequence of MOs and their

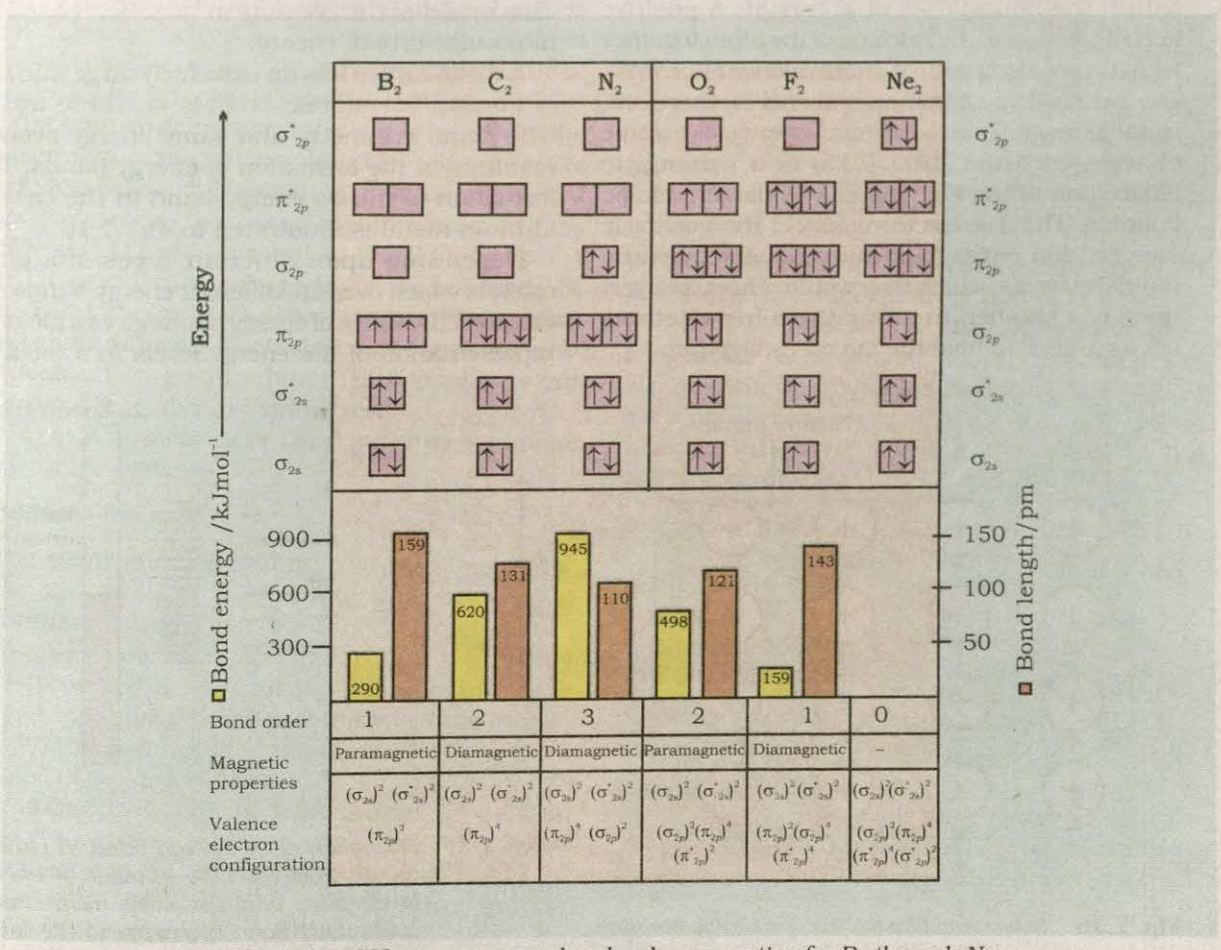


Fig. 1.14 *MO occupancy and molecular properties for B_2 through Ne_2.*

electron population are shown. The bond energy, bond length, bond order, magnetic properties and valence electron configuration appear below the orbital diagrams.

1.10 METALLIC BONDING

Metals, which constitute about three quarters of the elements, are characterized by bright luster, high electrical and thermal conductivity, malleability, ductility and high tensile strength. A metallic crystal consists of a very large number of atoms arranged in a regular pattern. Different models have been proposed to explain the nature of metallic bonding. Here we shall discuss two of these models:
(i) The Electron Sea Model (ii) The Band Model

1.10.1 The Electron Sea Model

In this model, a metal is assumed to consist of a lattice of positive ions (or kernels) immersed in a sea of mobile valence electrons, which move freely within the boundaries of a crystal. A positive kernel consists of the nucleus of the atom together with its core electrons (i.e., non-valence electrons). The net positive charge on a kernel is, therefore, equal in magnitude to the total valence electronic charge per atom. (Fig.1.15) is a schematic illustration of the electron sea model of metallic bonding. The free electrons shield the positively charged ion cores from mutual electrostatic repulsive forces, which they would otherwise exert upon one another. In a way these free electrons act as a 'glue' to hold the ion cores together.

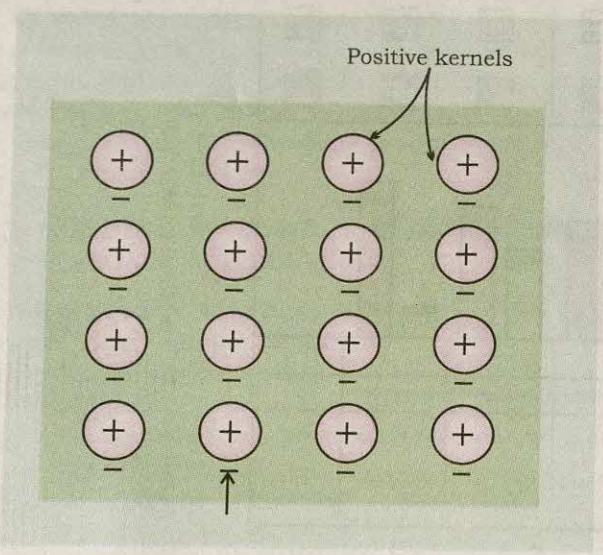


Fig. 1.15 *Schematic illustration of metallic bonding in 'electron sea model'.*

The forces that hold the atoms together in a metal as a result of the attraction between positive ions and surrounding freely mobile electrons are known as metallic bonds.

Though the electron sea model predated quantum mechanics, it still satisfactorily explains certain properties of the metals. The electrical and thermal conductivity of metals, for example, can be explained by the presence of mobile electrons in metals. On applying an electric field, these mobile electrons conduct electricity throughout the metal from one end to the other. Similarly, if one part of a metal is heated, the mobile electrons in that part of the metal acquire a large amount of kinetic energy. Being free and mobile, these electrons move rapidly throughout the metal and conduct heat to other parts of the metal. On the whole this model is not satisfactory.

1.10.2 The Band Model

This model of the bonding in metals is based on molecular orbital theory.

A metal lattice has an extremely large number of atoms. The atomic orbitals on these atoms with same symmetry and same energy overlap resulting in the formation of energy bands. The formation of the *2s* energy band in the case of Lithium metal is illustrated in Fig. 1.16.

Depending upon different types of atomic orbitals which overlap, different energy bands are obtained. This idea of energy bands gives a pictorial representation of the energy levels in a metallic

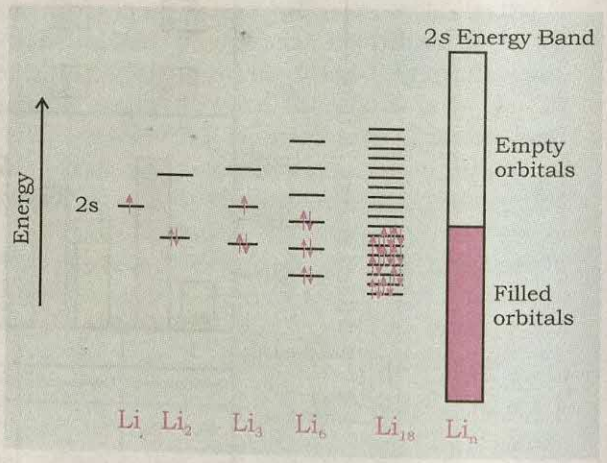


Fig. 1.16 *Formation of 2s energy band in Lithium metal. Note that the number of energy levels grow until the levels merge into a continuous band of energies. The lower half of the band is occupied by electrons.*

crystal. The arrangement of electrons in the different energy bands determines the characteristics of a metal. The energy bands formed from different atomic orbitals may overlap or be separated from each other. **The highest occupied energy band is called the valence band while the lowest unoccupied energy band is called the conduction band. The energy gap between the top of the valence band and the bottom of the conduction band is called the energy gap E_g.** In the case of metals, the valence band may be half filled or there may be an overlapping between the valence and the conduction bands. This makes it possible for the electrons to go into the vacant bands and hence is responsible for high electrical conductivity of metals.

In the case of **insulators**, the energy gap is very large and therefore the vacant conduction band is not available to the electrons of the completely filled valence band. Several solids have electrical properties intermediate between those of metals and insulators. These are called **semiconductors**. The energy gap in these substances is very small and increase in temperature gives thermal energy for some of the electrons in the valence band to move into the conduction band. The energy gap values in kJ/mol for the carbon group elements are: diamond (511), Silicon (111) and Germanium (63) (Fig. 1.17).

Diamond with a large E_g is an insulator. Si and Ge have fairly small band gaps and are called **semiconductors**. Their electrical conductivity is substantially greater than that of insulators but far less than that of conductors.

Let us now consider band structures of some metallic crystals.

Sodium Crystal

The electronic configuration of Na atom is $1s^2\ 2s^2\ 2p^6\ 3s^1$. Let us assume that the crystal contains N atoms where N is of the order of 10^{23}. We shall now consider the formation of energy bands in sodium crystal as a result of the linear combinations of the AOs of the N sodium atoms. The N *1s* sodium atomic orbitals shall form *1s* band, N *2s* atomic orbitals *2s* band, N *2p* atomic orbitals *2p* band and N *3s* atomic orbitals 3s band as shown in Fig. 1.18(a). *1s* energy band has a capacity of 2N electrons and therefore holds 2N *1s* electrons of N sodium atoms. Similarly the 2s and 2p bands shall be completely filled in sodium crystal.

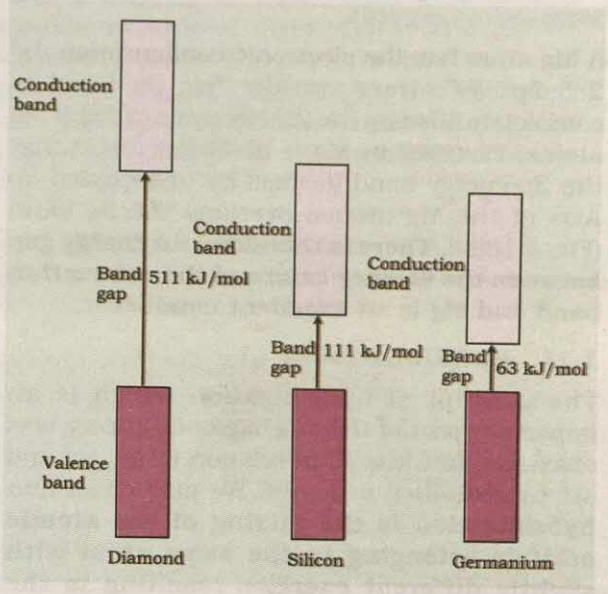


Fig. 1.17 *Energy bands in diamond, silicon and germanium. The band gap decreases from diamond to silicon to germanium. Diamond is an insulator; silicon and germanium are semiconductors. By warming silicon and germanium, electrons are excited from the valence band to the conduction band where they are free to move.*

The *3s* energy band too has a capacity of 2N electrons. But since there are only N *3s* electrons in the N sodium atoms, **the *3s* band is only half filled**. As mentioned above, the presence of electrons in the half filled *3s* band leads to high electrical conductance as a number of unoccupied energy levels are available in the valence band itself.

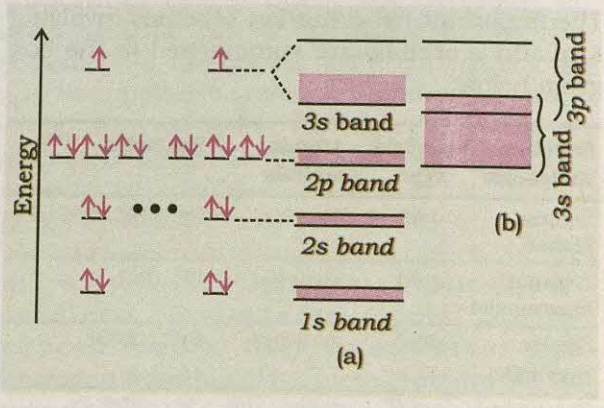


Fig. 1.18 *Formation of energy bands in (a) sodium crystal and (b) magnesium crystal.*

Magnesium crystal

A Mg atom has the electronic configuration $1s^2$ $2s^2$ $2p^6$ $3s^2$. Here, unlike Na, *3s* band is completely filled by the 2N electrons of the N Mg atoms. However in Mg it has been found that the *3p* energy band (formed by unoccupied *3p* AOs of the Mg atoms) overlaps the *3s* band (Fig. 1.18(b)]. **There is therefore, no energy gap between the valence band and the conduction band and Mg is an excellent conductor.**

1.11 HYBRIDIZATION

The concept of hybridization which is an important part of the valence bond theory was discussed in Class XI in relation to *sp*, sp^2 and sp^3 hybridization schemes. We may recall that **hybridization is the mixing of the atomic orbitals belonging to the same atom with slightly different energies resulting in the formation of new orbitals of equal energy and identical shapes. The new orbitals so formed are designated as hybrid-orbitals.**

Depending upon the number and type of atomic orbitals mixed, hybridization can be of several types. The shape of the molecule depends upon the state of hybridization of the central atom. Some examples of the molecules such as $BeCl_2$, BCl_3, CH_4, NH_3, H_2O, C_2H_4, C_2H_2 the shapes of which can be explained on the basis of *sp*, sp^2 or sp^3 hybridization have already been discussed in Class XI. Here we shall now take up a few examples of molecules whose shapes can be explained by hybridization schemes involving *s*, *p* and *d* orbitals.

1.11.1 Hybridization involving *s*, *p* and *d* orbitals

The important hybridization schemes involving *s*, *p* and *d* orbitals are summarized in the box given below:

Shape of molecules	Hybrid type	Atomic orbitals	Examples
Square planar	dsp^2	$d+s+2(p)$	$Ni(CN)_4]^{2-}$, $[PtCl_4]^{2-}$
Trigonal bipyramidal	sp^3d	$s+3(p)+d$	PF_5, PCl_5
Square pyramidal	dsp^3	$d+s+3(p)$	BrF_5, $XeOF_4$
Octahedral	sp^3d^2 d^2sp^3	$s+3(p)+2(d)$ $2(d)+s+3(p)$	SF_6, $[CrF_6]^{3-}$ $[Co(NH_3)_6]^{3+}$

The above hybridization schemes have mostly been invoked to explain the formation and structures of coordination compounds, with coordination numbers of the central atom/ion varying from 4 to 6 (see Unit10), and it also helps in explaining the formation of hypervalent compounds like PCl_5 and SF_6. Let us consider the formation of these compounds in more detail. The electronic configurations of phosphorus and sulphur show that the atoms of these elements have five and six electrons, respectively, in the *3s* and *3p* orbitals taken together. In their ground state, these atoms have (like nitrogen and oxygen) three and two half filled orbitals respectively. Thus, they form compounds like PF_3 and H_2S. Phosphorus and sulphur also form compounds like PF_5 and SF_6. Since NF_5 and OF_6 are not known, it follows that some **new feature is associated with the elements of the third period.** This feature is the availability of the *3d* oribitals which are comparable in energy to the occupied *3s* and *3p* orbitals. The paired electrons in the latter can, therefore, be unpaired by promotion to the vacant *3d* orbitals leading to covalencies of 5 and 6. Hybridization can now involve besides the *s* and *p* orbitals, the *d* orbitals also, yielding molecular geometries not found amongst compounds of the second period elements.

(i) Formation of PCl_5 (sp^3d Hybridization) The ground state electronic configuration of phosphorus atom (Z = 15) is represented as:

$$P = 1s^2 2s^2 2p^6 3s^2 3p^3$$
(ground state)

In order to explain the penta covalency of phosphorus it is assumed that under the conditions of bond formation the *3s* electrons get unpaired and one of it is promoted to the vacant $3d_{z^2}$ orbital. The excited state configuration of phosphorus being represented as:

$$P^* = 1s^2 2s^2 2p^6 3s^1 3p^3 3d^1$$
(excited state)

Now five orbitals, i.e., one *s*, three *p* and one *d* orbital are available for hybridization to yield a set of five sp^3d hybrid orbitals, which point towards the five corners of a trigonal-bipyramid (Fig. 1.19).

Three of these hybrid orbitals are oriented towards the three corners of an equilateral triangle making an angle of 120° between them. The remaining two hybrid orbitals are oriented at right angles to these three orbitals. In PCl_5,

these five sp^3d orbitals of phosphorus overlap with half-filled orbitals of chlorine atoms to form five P-Cl sigma bonds. Three P-Cl bonds lie in one plane and make an angle of 120° with each other. These bonds are called **equatorial bonds**. The remaining two P-Cl bonds are perpendicular to the plane of equotorial bonds i.e., one above and the other below the equitorial plane. These bonds are called **axial bonds**. As the axial bond pairs suffer more repulsive interactions from the equatorial bond pairs, therefore, the axial bonds are slightly elongated and hence slightly weaker than the equatorial bonds. *This makes PCl_5 quite reactive.*

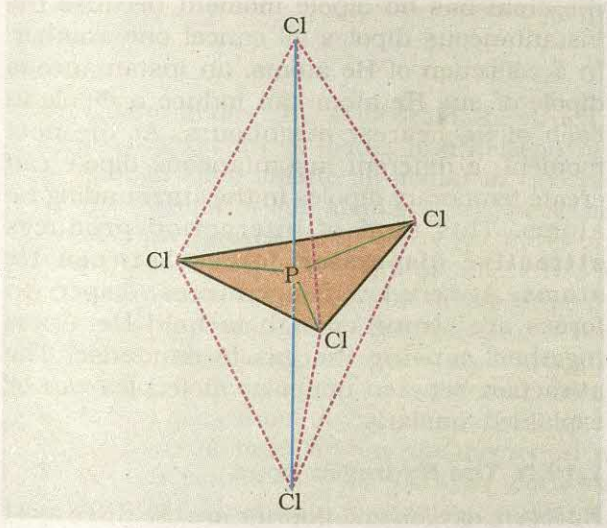


Fig. 1.19 *Trigonal bipyramidal geometry of PCl_5 molecule.*

(ii) Formation of SF_6 (sp^3d^2 Hybridization) The ground and excited state configurations of sulphur are represented as :

$$S = 1s^2 2s^2 2p^6 3s^2 3p^4$$
(ground state)

$$S^* = 1s^2 2s^2 2p^6 3s^1 3p^3 3d^2$$
(excited state)

In the excited state the available six orbitals i.e., one *s*, three *p* and two *d* are half-filled. These hybridize to form six new sp^3d^2 hybrid orbitals which are projected towards the six corners of a regular octahedron. In SF_6, these six sp^3d^2 hybrid orbitals overlap with half-filled orbitals of fluorine atoms to form six S-F sigma bonds and SF_6 has a regular octahedral geometry as shown in Fig. 1.20. All the six S-F bonds in SF_6 have same bond length.

For a number of theoretical reasons and considerations of energetics, the above explanation for bonding in hypervalent molecules like (PCl_5 and SF_6) is not accepted now. The bonding in hypervalent molecules is best explained in terms of MO theory (Page 170).

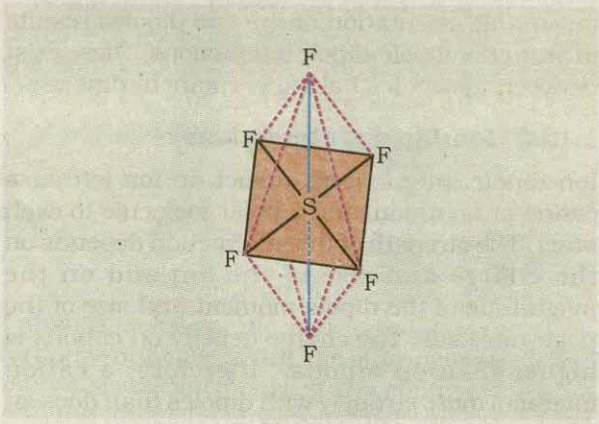


Fig. 1.20 *Octahedral geometry of SF_6 molecule.*

1.12 INTERMOLECULAR FORCES

The forces between the molecules of a substance are known as ***intermolecular forces***. Such forces exist in all states of matter and are responsible for many structural features and physical properties of matter. The ***intramolecular forces*** on the other hand exist within each molecule (or polyatomic ion) and influence the chemical properties of the substance.

Intermolecular forces are weak forces. It usually requires , for example, much less energy to evaporate a liquid than to break the bond in the molecules of the liquid. The boiling points of substances often reflect the strength of intermolecular forces operating among the molecules. At the boiling point, enough energy must be supplied to overcome the attractive forces among molecules before the substance can enter into vapour phase. Similarly, the melting point of substances increase with increase in the strength of the intermolecular forces.

Intermolecular forces arise due to the following types of interactions: **Dipole-dipole, Ion–dipole, Ion-induced dipole, Dipole-induced dipole, Dispersion forces and Hydrogen bonding. The term 'van der Waals forces' refers to dipole-dipole, dipole-induced dipole and dispersion forces.** Depending on the

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phase of the substance, the nature of chemical bonds and the types of element present, more than one type of interaction may contribute to the total attraction between molecules.

1.12.1 Dipole-Dipole Interactions

Dipole-dipole interactions depend upon the distance and orientation of the two dipoles. A favourable orientation of the two dipoles results in attractive dipole-dipole interactions. These exist between molecules having permanent dipoles.

1.12.2 Ion-Dipole Interactions

Ion-dipole interactions attract an ion (either a cation or an anion) and a polar molecule to each other. The strength of this interaction depends on the charge and size of the ion and on the magnitude of the dipole moment and size of the polar molecule. The charge density on cations is higher than on anions, therefore, a cation interacts more strongly with dipoles than does an anion having same charge but bigger size. **Hydration of different ions is an example of ion-dipole interaction**: In an aqueous NaCl solution, the Na^+ and Cl^- ions are surrounded by water molecules, which have a large dipole moment. When an ionic compound like NaCl dissolves, the water molecules act as a dielectric to keep the ions apart. On the other hand, carbon tetrachloride (CCl_4), a nonpolar molecule lacks the ability to participate in ion-dipole interaction. Therefore, carbon tetrachloride is a poor solvent for ionic compounds, as are most nonpolar liquids.

1.12.3 Ion-Induced Dipole Interactions and Dipole-Induced Dipole Interactions

The attractive interaction between an ion and the induced dipole is called ion-induced dipole interaction, and the attractive interaction between a polar molecule and the induced dipole is called dipole-induced dipole interaction. The likelihood of a dipole moment being induced depends not only on the charge on the ion or the strength of the dipole but also on the polarizability of the atom or molecule i.e., the ease with which the electron distribution in the atom (or molecule) can be distorted.

1.12.4 Dispersion Forces

Dispersion forces are the attractive forces between nonpolar substances such as O_2, N_2 or monoatomic gases such as He, Ne, Ar etc. These arise as a result of instantaneous dipoles created in these nonpolar molecules or atoms. Let us understand the origin of these forces, say in helium gas. In a helium atom the electrons are moving at some distance from the nucleus. At any instant it is likely that the atom has a dipole moment created by the specific positions of electrons. **This dipole moment is called an 'instantaneous dipole' because it lasts for just a fleeting moment.** In the next instant the electrons are in different locations and the atom has a new instantaneous dipole, and so on. Averaged over time (that is, the time it takes to make a dipole moment measurement), however, the atom has no dipole moment because the instantaneous dipoles all cancel one another. In a collection of He atoms, an instantaneous dipole of one He atom can induce a dipole in each of its nearest neighbours. At the next moment, a different instantaneous dipole can create temporary dipoles in the surrounding He atoms. This kind of interaction produces **attractive dispersion forces between He atoms.** At very low temperatures, dispersion forces are strong enough to hold He atoms together, causing the gas to condense. The attraction between nonpolar molecules can be explained similarly.

1.12.5 The Hydrogen Bond

Nitrogen, oxygen and fluorine are the three most electronegative elements. When they are attached to a hydrogen atom, the electrons are drawn towards the electronegative atom.

This H atom attached to nitrogen, oxygen or fluorine is able to interpose itself between two such electronegative atoms bonding them together. This is called hydrogen bond.

The essential requirements for a H–bond are :

(i) a hydrogen atom attached to a highly electronegative atom;

(ii) a lone pair of electrons on the electronegative atom.

The hydrogen bond is written as

A—H...B or A—H...A

where A and B represent O, N, or F; A – H is one molecule or part of a molecule and B is a part of another molecule and the **dotted line represents the hydrogen bond**. The three atoms usually lie in a straight line, but the angle AHB (or AHA) can deviate as much as 30° from

linearity. **Note that the O, N and F atoms all possess at least one lone pair of electrons that can interact with the hydrogen atom in hydrogen bonding.**

The energy of a hydrogen bond is of the order 40 kJ/mol. **Hydrogen bonds have a powerful effect on the structures and properties of many compounds.**

The boiling points of a series of similar compounds containing elements in the same periodic group normally increase with increasing molar mass. The hydrogen compounds of the elements in Groups 15, 16 and 17 do not follow this trend. In each of these series, the lightest compound (NH_3, H_2O, HF) has the highest boiling point, contrary to expectations based on molar mass. The reason is that there is extensive hydrogen bonding between molecules in these compounds.

Some unique properties of water such as the density of ice being less than that of water and the contraction of water when heated between 0°C and 4°C can also be explained on the basis of hydrogen bonding.

SUMMARY

Quantum mechanical model of the structure of atom is based on the principles of wave-particle duality of matter and Heisenberg uncertainly principle. Both these principles, though applicable to all matter in motion, assume significance only in the context of microscopic or sub-atomic particles. According to the principle of wave-particle duality of matter, waves known as matter waves or de Broglie waves are associated with moving particles. The wavelength of such waves associated with a particle of mass m moving with velocity v is given by the de Broglie relation $\lambda = h/mv$. Heisenberg uncertainty principle is a consequence of the dual behavior of matter and radiation. According to this principle, it is impossible to determine simultaneously both the position and momentum of a moving particle with certainty. An important consequence of the Heisenberg uncertainty principle is that one cannot determine the path of a moving microscopic particle.

Quantum mechanics is the theoretical science of microscopic matter. It specifies the laws of motion that microscopic particles obey. Its central equation is Schrodinger equation. Quantum mechanical study of any system involves four steps : (i) Writing Schrodinger equation (ii) Specifying the boundary conditions of the system (iii) Solving Schrodinger equation to obtain Ψ and E (iv) Calculating all the observable properties of the system from Ψ.

The solution of the Schrodinger equation of the hydrogen atom gives the possible energy states of the electron and the corresponding wave functions , also known as atomic orbitals. These atomic orbitals can also be used with a reasonable accuracy in multi-electron atoms. An atomic orbital is a one electron wave function (Ψ) that defines the distribution of electron density ($|\Psi|^2$) in space. Orbitals can be represented by charge cloud diagrams or boundary surface diagrams.

There are two quantum mechanical theories of covalent bond formation : valence bond theory and molecular orbital theory. Molecular orbital theory describes bonding in terms of the combination and arrangement of atomic orbitals to form molecular orbitals that are associated with the molecule as a whole. The number of molecular orbitals always equals the number of atomic orbitals that were combined. Bonding molecular orbitals increase electron density between the nuclei and are lower in energy than the individual atomic orbitals. Antibonding molecular orbitals have a region of zero electron density between the nuclei and an energy level higher than that of the individual atomic orbitals.

The electronic configuration of the molecules is written by filling electrons in the molecular orbitals in the order of increasing energy levels . As in the case of atoms, the Pauli exclusion principle and Hund's rule govern the filling of molecular orbitals. Molecules are said to be stable if the number of electrons in bonding molecular orbitals is greater than that in antibonding molecular orbitals.

Metallic bonds can be thought of as the force between positive ions immersed in a sea of electrons. In terms of band theory, atomic orbitals merge to form energy bands. A substance is a conductor when the electrons can be readily promoted to the conduction band where they are free to move through the substance. In insulators, the energy gap between the valence band and the conduction band is so large that the electrons cannot be promoted to the conduction band. In semiconductors, electrons can cross the energy gap at high temperatures and thus conductivity increases with increasing temperature as more electrons are able to reach the conduction band.

Hybridization is a concept of the valence bond theory. Hybridized atomic orbitals are formed by the combination and rearrangement of atomic orbitals from the same atom. The hybridized orbitals are all of equal energy and their number is equal to the number of pure atomic orbitals that combine.

Intermolecular forces act between molecules or between molecules and ions. Generally these forces are much weaker than the bonding forces. Dipole-dipole forces and ion-dipole forces attract molecules with dipole moments to other polar molecules or ions. Dispersion forces are the result of temporary dipoles induced in the ordinarily nonpolar molecules. The term 'van der Waals forces' refers to dipole-dipole, dipole-induced dipole and dispersion forces.

EXERCISES

1.1 What are the dimensions of Planck constant? What other physical quantity has the same dimension.

1.2 What experimental support is available for de Broglie's concept?

1.3 Two particles A and B are in motion. If the wavelength associated with particle A is 5×10^{-8} m, calculate the wavelength associated with particle B if its momentum is half of A.

1.4 Calculate the wavelength of 1000 kg rocket moving with a velocity of 3000 km per hour. ($h = 6.626 \times 10^{-34}$ Js)

1.5 The sodium flame test has a characteristic yellow colour due to emissions of wavelength 589 nm. What is the mass equivalence of one photon of this wavelength?

1.6 Calculate the uncertainty in the velocity of a wagon of mass 2000 kg whose position is known to an accuracy of $\pm$ 10m.

1.7 Calculate the uncertainty in position of a dust particle with mass equal to 1 mg if the uncertainty in its velocity is 5.5×10^{-20} ms^{-1}.

1.8 On the basis of Heisenberg uncertainty principle, show that electron cannot exist within the atomic nucleus (radius = 10^{-15} m), $h = 6.626 \times 10^{-34}$Jsec. (Hint: since the calculated value of Δv comes out to be much higher than the velocity of light, the electron cannot exist within the atomic nucleus.)

1.9 Why can't we overcome the uncertainty predicted by Heisenberg's principle by building more precise devices to reduce the error in measurement below the $h/4\pi$ limit?

1.10 What physical meaning is attributed to the square of the absolute value of wave function $|\Psi|^2$?

1.11 Which of the four quantum numbers (n, l, m_l, m_s) determine (a) the energy of an electron in a hydrogen atom and in a many-electron atom, (b) the size of an orbital, (c) the shape of an orbital, (d) the orientation of an orbital in space?

1.12 Draw the shapes (boundary surfaces) of the following orbitals: (a) $2p_y$, (b) $3d_{z^2}$, (c) $3d_{x^2-y^2}$. (Show coordinate axes in your sketches.)

1.13 Discuss the similarities and differences between a $1s$ and a $2s$ orbital.

1.14 For each of the following pair of hydrogen orbitals, indicate which is higher in energy: (a) *1s*, *2s*; (b) *2p*, *3p*; (c) $3d_{xy}$, $3d_{yz}$; (d) *3s*, *3d*; (e) *4f*, *5s*.

1.15 Which orbital in each of the following pairs is lower in energy in a many-electron atom? (a) *2s*, *2p*; (b) *3p*, *3d*; (c) *3s*, *4s*; (d) *4d*, *5f*.

1.16 Explain the meaning of the symbol $4d^6$.

1.17 The ground-state electron configurations listed here are incorrect. Explain what mistakes have been made in each and write the correct electron configurations.

Al : $1s^2 2s^2 2p^4 3s^2 3p^3$

B: $1s^2 2s^2 2p^5$

F: $1s^2 2s^2 2p^6$

1.18 Draw orbital diagrams for atoms with the following electronic configuration:
(a) $1s^2 2s^2 2p^5$ (b) $1s^2 2s^2 2p^6 3s^2 3p^3$ (c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$

1.19 What do you understand by (i) Radial probability density, R^2 and (ii) Radial probability function, $4\pi r^2 R^2$? How do they vary with r for *1s*, *2s* and *2p* atomic orbitals of hydrogen atom?

1.20 Two *p* orbitals from one atom and two *p* orbitals from another atom are combined to form molecular orbitals. How many MOs will result from this combination? Explain.

1.21 Show the shapes of bonding and antibonding MOs formed by combination of (a) two s orbitals (b) two *p* orbitals (side to side).

1.22 How do the bonding and antibonding MOs formed from a given pair of AOs compare to each other with respect to (a) energy (b) presence of nodes (c) internuclear electron density?

1.23 Arrange the following species in order of increasing stability: Li_2, Li_2^+, Li_2^-.
Justify your choice with a molecular orbital energy level diagram.

1.24 Use molecular orbital theory to explain why the Be_2 molecule does not exist.

1.25 Explain why the bond order of N_2 is greater than N_2^+, but the bond order of O_2 is less than that of O_2^+.

1.26 Compare the relative stability of the following species and indicate their magnetic properties (diamagnetic or paramagnetic); O_2, O_2^+, O_2^-(superoxide), O_2^{2-} (peroxide ion).

1.27 Explain the significance of bond order. Can bond order be used for quantitative comparisons of the strengths of chemical bonds?

1.28 What is the energy gap in band theory? Compare its size in conductors, semiconductors and insulators.

1.29 Which of the following substances exhibit H-bonding? Draw the H bonds between two molecules of the substance where appropriate:

(a) CH_3CH_2OH

(b) $CH_3-\overset{\overset{O}{\|}}{C}-OH$

(c) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(d) $CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

1.30 How can one nonpolar molecule induce a dipole in a nearby nonpolar molecule?

1.31 What type(s) of intermolecular forces exist between the following pairs? (a) HBr and H_2S, (b) Cl_2 and CBr_4, (c) I_2 and NO_3^-, and (d) NH_3 and C_6H_6?
(Hint: To identify intermolecular forces, it is useful to classify the species being considered as (1) nonpolar molecules, (2) polar molecules, and (3) ions. Keep in mind that dispersion forces exist between all species.)

UNIT 2

THE SOLID STATE

OBJECTIVES

After studying this Unit, you will be able to:

- classify solids on the basis of binding forces
- understand structure of solids and define unit cell, lattice and describe packing including efficiency of packing
- determine various dimensional parameters using X-ray diffraction
- explain the structures of various solids and predict the structures of ionic solids by applying the ionic radii ratio rule
- describe the imperfections in solids and their effects on the properties
- describe the applications of solids in industries based on their electrical, magnetic and dielectric properties
- distinguish crystalline solids from amorphous solids

"The infinite variety in the properties of solid materials we find in the world is really the expression of the infinite variety of the ways in which the atoms and molecules can be tied..." - *Rudolf Clausius*

We are mostly surrounded by solid objects and would like to know more about them. Discovering new solid materials is one of the most active areas of research in modern science and technology. Materials like high temperature superconductors, biocompatible solids (for surgical implants) and a host of other solid complex materials are destined to play an ever expanding role in future development of science and society.

From our earlier studies (Class XI) we know that gases and liquids belong to **fluid state**. The fluidity of liquids and gases is determined by the relative free motion of their molecules. In solids, on the contrary, molecules/atoms/ions are not free to move but can oscillate around their fixed positions due to strong intermolecular/interatomic/interionic forces. This confers rigidity and **long range order** in solids.

In this Unit, we shall discuss some of the arrangements of atoms, molecules and ions in solids and explore the reasons why one arrangement is preferred to another. Different arrangements lend different properties to the solids. Some of these classified properties are affected even by the presence of traces of impurities.

2.1 CLASSIFICATION OF SOLIDS

Solids are broadly classified as *crystalline* and *amorphous*. In a crystalline solid, -atoms, ions, or molecules are held in an orderly array. In amorphous solid there is only **short range order**, otherwise constituent species are disordered. Thus rapidly solidified liquids are amorphous materials e.g. glass, amorphous silica etc. Amorphous solids will be discussed at the end of this Unit.

Most of the substances (elements and compounds) form crystalline solids. Elements

like iron, copper, silver, sulphur, phosphorous and iodine, and compounds such as sodium chloride, potassium nitrate all form crystals. Some substances adopt different structural arrangements under different conditions. Such arrangements are called **polymorphs**. Thus, diamond and graphite are two different polymorphic forms of carbon. These different structures have different properties, such as melting point and density. Graphite is soft and a good conductor of electricity whereas diamond is hard and a poor conductor of electricity. The specific arrangement of atoms, ions or molecules within a crystal can be determined by X-ray diffraction studies which you will study in Section 2.3.

Crystalline solids based on the nature of bonding are classified into four main categories viz. covalent, ionic, metallic and molecular solids. Table 2.1 provides examples of different types of solids. The physical properties like standard molar enthalpy of fusion, electrical and thermal conductivity provide information to which of these four categories the solid belongs.

2.2 DETERMINATION OF STRUCTURE OF SOLIDS

In general, the structure of solids is determined by diffraction methods. However, X-ray diffraction has been used more extensively for this purpose.

2.2.1 Structure Determination by X-ray Diffraction

If we look through a piece of a thin stretched cloth against bright light, we find a pattern caused by deflection of light as it passes through the regularly spaced threads of the fabric. This deflection of light is called **diffraction** and the patterns produced are called *diffraction patterns*. From the diffraction pattern, it is possible to deduce the arrangements of strands in the fabric. The same idea is used to determine the arrangement of atoms/ions in a crystal. Max von Laue visualised that a crystal can act as three dimensional grating for the diffraction of X-rays. In 1912 he obtained a diffraction pattern produced by passing X-rays through a crystal of copper sulphate. W.L. Bragg and his father W.H. Bragg determined the cubic structure of sodium chloride using X-rays. These days, the structures of extremely complex substances such as proteins and nucleic acids are determined using this technique.

When a beam of X-rays falls on a crystal plane composed of regularly arranged atoms or ions, the X-rays are diffracted. Waves from the diffracted X-rays may interfere and destroy each other (Fig. 2.1). However, it is also possible that X-rays diffracted by the particles (atoms/ions) can also reinforce each other producing constructive interference.

Table 2.1 Different Types of Solids

Type of solid	Constituent particles	Bonding/ Attractive forces	Approximate binding energy/ $kJmol^{-1}$	Examples	Physical nature	mp/K	Electrical conductivity
Molecular	Molecules	i) Dispersion	0.05-40	Argon	Soft	84	Insulator
		ii) Dipole interaction	5-25	HCl	Soft	158	Insulator
		iii) Hydrogen Bonding	10-40	H_2O(ice)	Hard	273	Insulator
Metallic	Atoms	Positive ions and electrons (delocalized electrons)	70-1000	Ag, Cu, Mg	Hard	~ 800 to 1000	Conductor
Network or Covalent	Atoms	Covalent	150-500	SiO_2, SiC, C(diamond)	Hard	~ 4000	Insulator
Ionic	Ions	Coulombic or electrostatic	400-4000	NaCl, MgO, KCl, $BaCl_2$	Hard but brittle	High ~ 1500	Insulator

William H. Bragg

W. Lawrence Bragg

William H. Bragg after graduation from University of Cambridge became professor of Physics at the University of Adelaide (Australia) at the age of twenty three and returned to the University of Leeds, England in 1909. His son, W. Lawrence Bragg (born in 1890) also graduated from Cambridge. Being inspired by Max von Laue's work on X-rays, William discussed X-rays diffraction with his son Lawrence when he (Lawrence) was at the age of eighteen and studying at the University of Cambridge. Lawrence worked out the theory of X-rays diffraction what is today known as **Bragg equation**. Father and son jointly deduced structures of several ionic crystals and in 1915 shared Nobel prize for Physics. They are the only father and son team to have received this honour and Lawrence is also the youngest person to have received it.

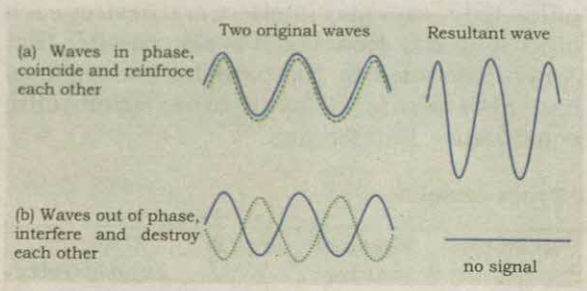


Fig. 2.1 *Constructive and destructive interference of X-rays.*

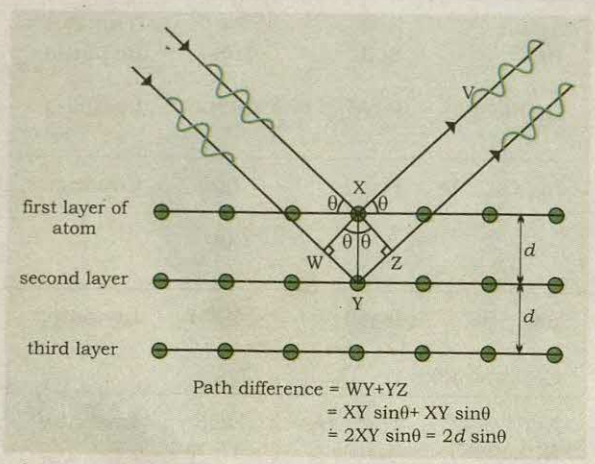


Fig. 2.2 *The diffraction of two waves of X-rays by the regularly spaced atoms in a crystal.*

In Fig. 2.2, X-ray beams are shown to fall on planes of a crystal (such as sodium chloride). Only three planes of the crystal are shown in this figure. From the figure we can see that two waves in phase are approaching the crystal and after reflection, the ray emerging along XV is ahead of the ray emerging along YZ. Why is it so? How much further does the ray reflected at the second layer travel? If the waves are in phase after reflection, the difference in distance travelled by the two rays (i.e., *path difference)* must equal an integral number of wavelength, $n\lambda$, for constructive interference.

Thus, path difference = WY + YZ

$= XY \sin\theta + XY \sin\theta$

$= 2XY \sin\theta = 2d \sin\theta$

where d is the distance between two planes (layers). Therefore, for reinforcement of the reflected X-rays,

$$n\lambda = 2d \sin\theta \qquad (2.1)$$

Equation (2.1) is known as **Bragg equation**. For X-rays of a particular wavelength, λ, and for a given value of d, maximum reinforcement will occur only at certain values of θ. If we know value of θ and λ, we can calculate the distance, d, between planes in the crystal. By varying θ from 0° to 90°, one will obtain a series of reinforced strong signals (Fig. 2.3) from different sets of planes with different d values interspersed with regions of cancellation (due to destructive interference). In the Eq. (2.1), n is a positive integer (n = 1,2, 3, ... and so on) and represents order of reflection. The reflection angles increase with increasing order,

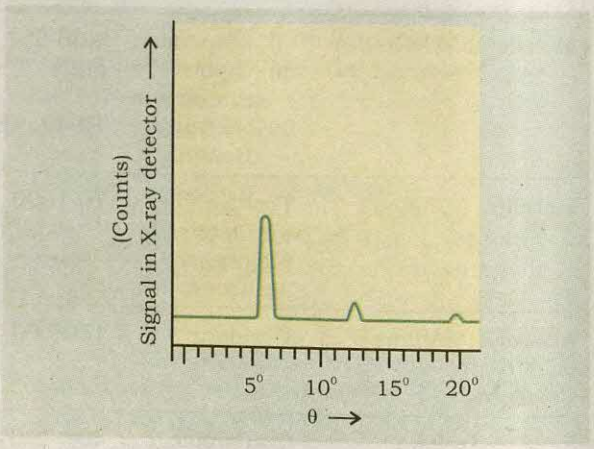


Fig. 2.3 *Signals from a crystal of sodium chloride as the angle between the direction of X-ray beam and the crystal face increases.*

n = 1, 2, 3..... We can get a lot of information about the structure of the crystal from these X-ray diffraction patterns. Crystal structure can be best described and systematised in terms of lattices and unit cells. These are described in the following section.

Example 2.1

A sample of a crystalline solid scatters a beam of X-rays of wavelength 70.93 pm at an angle 2θ of 14.66°. If this is a second order reflection (n = 2), calculate the distance between the parallel planes of atoms from which the scattered beam appears to have been reflected.

Solution

We know that $n\lambda = 2d \sin\theta$

$2\theta = 14.66°$ or $\theta = 7.33°$

$\lambda = 70.93\ pm = 70.93 \times 10^{-12}$ m

Therefore,

$$d = \frac{n\lambda}{2\sin\theta} = \frac{2 \times 70.93 \times 10^{-12}\ \text{m}}{2 \sin 7.33}$$

$$= 556.3 \times 10^{-12}\ \text{m}$$

$$= 556.3\ \text{pm}$$

2.3 LATTICES AND UNIT CELLS

Space lattice is a *regular repeating arrangement of points in space and forms the basis of classification of all structures.* For the sake of simplicity, we just discuss two dimensional arrangement of points called *two dimensional lattice* (Fig. 2.4).

There are five types of two dimensional lattices (Fig. 2.4). They are hexagonal, square, rectangular, rhombic and parallelogram lattices. These differ in symmetry of the arrangement of points.

A two dimensional lattice is a regular arrangement of the points, we need only to describe a small part of the lattice in order to specify it completely. We choose four points in two dimensional lattice and connect them to give a parallelogram. This figure is known as **Unit Cell.** *We can generate the full lattice by repeatedly moving the Unit Cell in the direction of its edges by a distance equal to the cell edge (Fig . 2.5).* Unit cell for any given lattice can be chosen in many different ways, and may include some cell that has interior points. The smallest unit cell

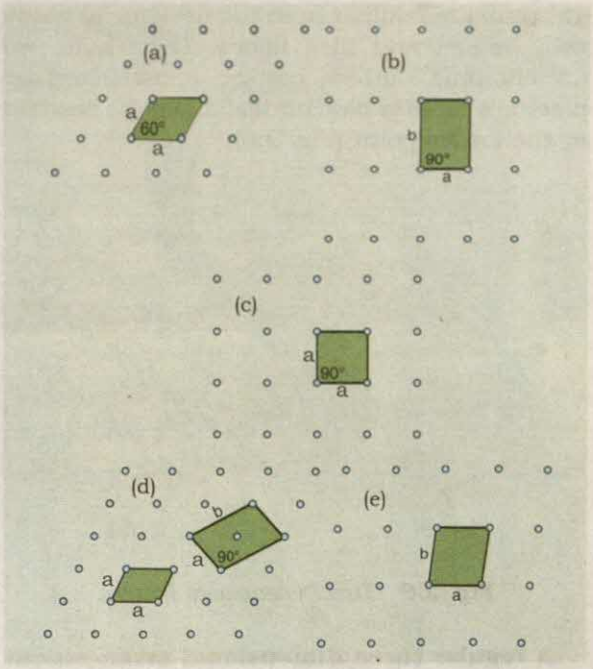


Fig. 2.4 *The five two dimensional lattices.*

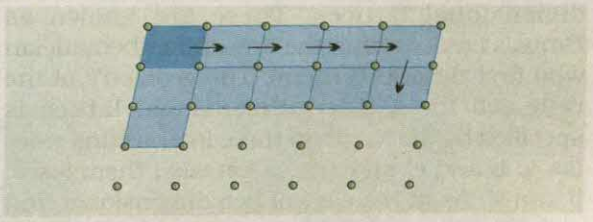


Fig. 2.5 *We can generate entire two dimensional lattice by repeatedly moving the unit cell in the direction of cell edges by distance equal to cell edge.*

that shows the full symmetry of the lattice is supposed to be the most convenient. For the square, the rectangular, and parallelogram lattices, the unit cells normally chosen are the square, the rectangle and the parallelogram. However, for a hexagonal lattice, a rhombus with an angle of 60° is chosen as the unit cell.

A unit cell with an interior point is called a **Centred Unit Cell**. In the case of rhombic lattices a centred rectangular unit cell is chosen. The unit cell that does not contain any interior point is known as a **Primitive Unit Cell**. Thus, we see that for describing a two dimensional lattice, we must specify the unit cell by *length of its edges and the angle between them.* Two dimensional

patterns are familiar from the designs on many wall papers and tiled floors. The whole two dimensional pattern can be constructed by placing a motif (a blue bird) at a definite position at the lattice point (Fig. 2.6).

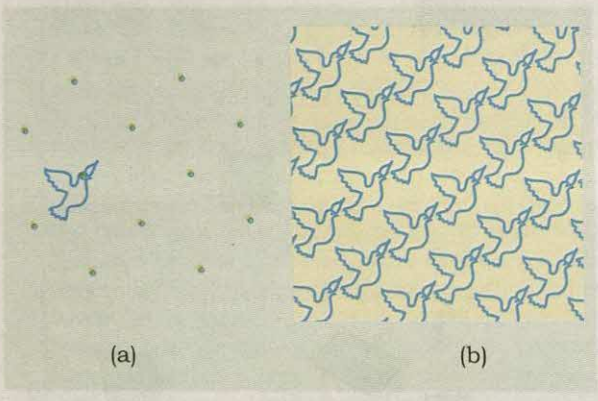


Fig. 2.6 *Two Dimensional Pattern.*

A regular three dimensional arrangement of points in space is called a space lattice. Just as there are 5 possible two dimensional lattices, there are only 14 possible three dimensional lattices. These are known as *Bravais Lattices* (after the French mathematician who first described them). The geometry of the unit cell for a three dimensional lattice is specified by the length of three intersecting sides (as a, b and c) and angles between them (as α, β and γ). As in the case of two dimensional unit cells, if we move a three dimensional unit cell by a distance equal to its edges along the three directions, we get a three dimensional crystal lattice (Fig. 2.7). Characteristics of seven **primitive unit cells** are listed in the Table 2.2 and these cells are shown in (Fig. 2.8).

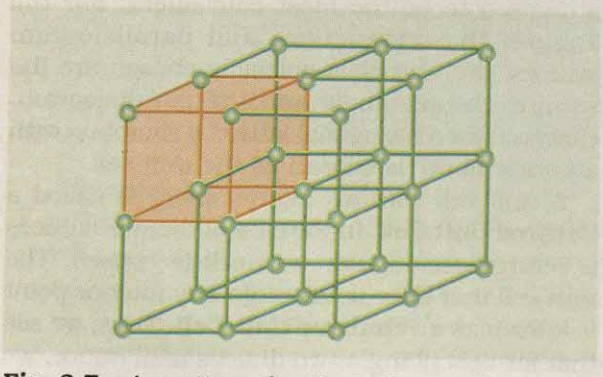


Fig. 2.7 *A portion of a three dimensional cubic lattice and its unit cell.*

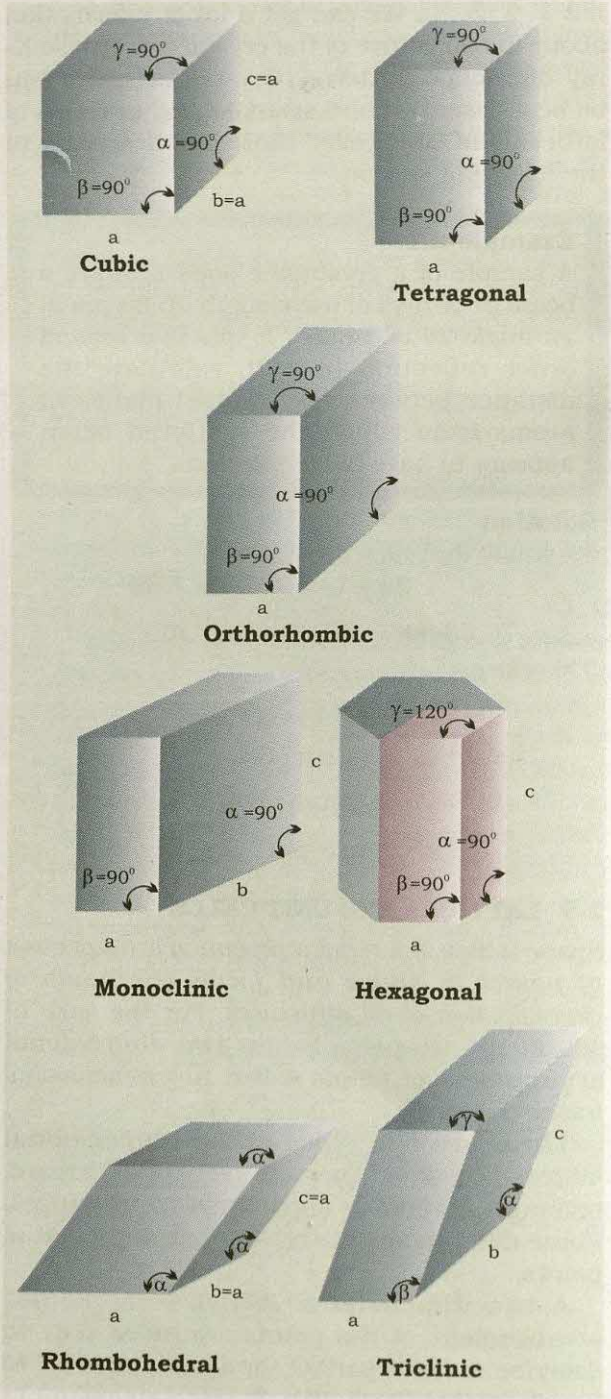


Fig. 2.8 *Seven primitive unit cells in crystals.*

The unit cell of the primitive cubic lattice is a cube. The unit cell of the *body centred cubic lattice* is a cube with an additional point in the centre. The unit cell of a *face centred cubic lattice* is a cube with an additional point in the centre of each face (Fig. 2.9).

Table 2.2 Seven Primitive Unit Cells

Crystal System	Axial distances or Edge lengths	Axial angles	Examples
Cubic	a = b = c	$\alpha=\beta=\gamma=90°$	Copper, Zinc blende, KCl
Tetragonal	a = b ≠ c	$\alpha=\beta=\gamma=90°$	Sn (White tin), SnO_2, TiO_2
Orthorhombic	a ≠ b ≠ c	$\alpha=\beta=\gamma=90°$	Rhombic sulphur, $CaCO_3$
Monoclinic	a ≠ b ≠ c	$\alpha=\gamma=90°;\beta\neq 90°$	Monoclinic sulphur, $PbCrO_2$
Hexagonal	a = b ≠ c	$\alpha=\beta=90°;\gamma=120°$	Graphite, ZnO
Rhombohedral	a = b = c	$\alpha=\beta=\gamma\neq 90°$	$CaCO_3$(Calcite), HgS(Cinnabar)
Triclinic	a ≠ b ≠ c	$\alpha\neq\beta\neq\gamma\neq 90°$	$K_2Cr_2O_7$, $CuSO_4.5H_2O$

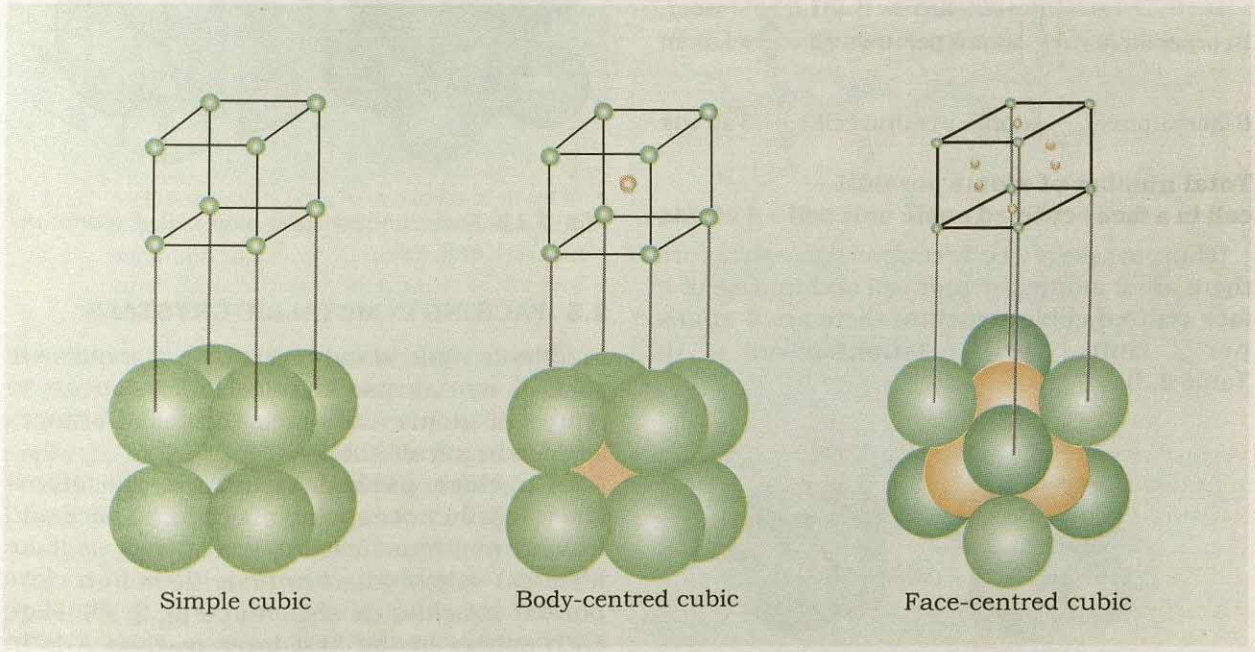


Fig. 2.9 *Three different types of cubic unit cells. The top row shows the lattice points of the cells. In the bottom row, the points are replaced with space-filling spheres representing the atoms or ions of the crystal. All spheres–no matter what their colour-represent identical atoms or ions centred on the lattice points. Here, the spheres at the corners of the body centred and face centred cubes do not touch each other. Rather, each corner atom in the body centered cell touches the central atom, and each corner atom in the face centered cell touches spheres in three adjoining faces.*

2.4 NUMBER OF ATOMS IN A UNIT CELL

2.4.1 Calculation of Number of Atoms Per Unit Cell

In a crystal, each corner of a unit cell is common to eight unit cells, its each edge to four unit cells and its each face to two unit cells. Consequently, if there is an atom, ion or molecule associated with each lattice point to give the crystal, then it contributes only 1/8 for the corner, 1/4 for the edge and 1/2 for the face. For the sake of simplification, here we shall consider only those cases in which each point in the unit cell is associated with one atom.

In case of a **primitive cubic unit cell**, there are eight corner atoms that are shared between eight unit cells. Therefore,

$$8\,\text{corners} \times \left(\frac{1}{8}\right)\text{atoms per unit cell} = \frac{8}{8} = 1\,\text{atom}$$

i.e., there is only one atom per unit cell in a **simple cubic** structure (Fig. 2.10).

In case of **body centred cubic** unit cell (Fig. 2.11):

$$8\,\text{corners} \times \left(\frac{1}{8}\right)\text{atoms per unit cell} = \frac{8}{8} = 1\,\text{atom}$$

$$1\,\text{centre atom per unit cell} = 1\,\text{atom}$$

$$\text{Total} = 2\,\text{atoms}$$

In case of **face centred cubic unit cell** (Fig. 2.12):

$$8\,\text{corner atoms} \times \left(\frac{1}{8}\right)\text{atoms per unit cell} = \frac{8}{8} = 1\,\text{atom}$$

$$6\,\text{face atoms} \times \left(\frac{1}{2}\right)\text{atoms per unit cell} = \frac{6}{2} = 3\,\text{atoms}$$

Total number of atoms per unit cell in a face centered cubic unit cell = 4 atoms

Thus, in case of a body centred cubic structure there are 2 atoms per unit cell and in case of a face centred cubic structure there are 4 atoms per unit cell (summarized in Table 2.3).

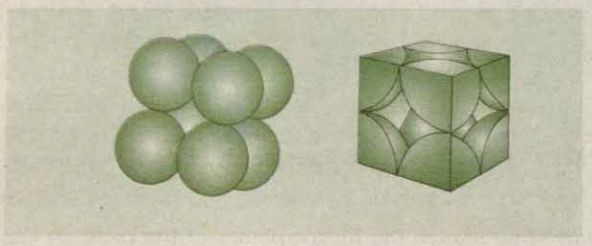


Fig. 2.10 *Space-filling representation of cubic unit cell, corner atom is being shared among eight unit cell.*

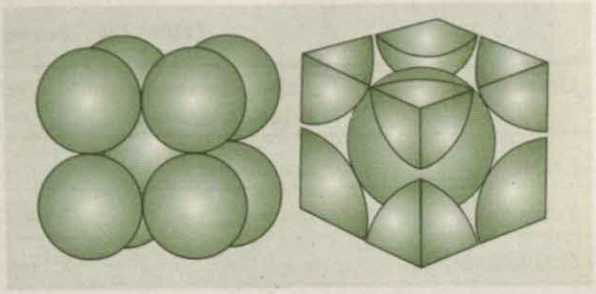


Fig. 2.11 *Body centred cubic unit cell–2 atoms per unit cell.*

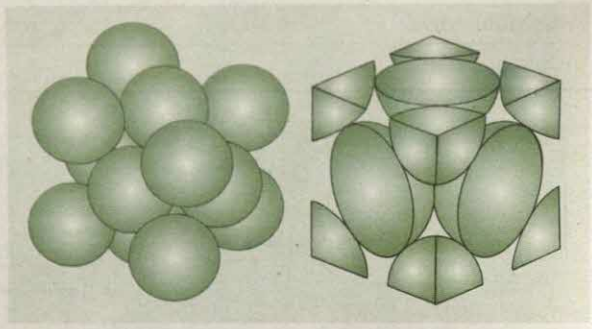


Fig. 2.12 *Face centred cubic unit cell–4 atoms per unit cell.*

2.5 PACKING IN METALLIC CRYSTALS

In order to understand how atoms in metals are packed, we can use identical hard spheres to represent atoms and stack them like oranges as seen in a fruit shop.

In a **close packed structure**, the atoms stack together occupying maximum space and leaving minimum vacant space. Let us take identical spheres *and arrange them in a close packed structure as shown in* (Fig. 2.13). Here each sphere in the first layer marked A is in contact with six neighbours. Now while arranging the second layer (say B) on the top of the first layer, spheres are placed in the depressions of the first layer.

Table 2.3 Number of atoms per unit cell

Type of Cell	Number of atoms at corners	Number of atoms in faces	Number of atoms in centre of cube	Total
Primitive cubic	$8\times1/8=1$	0	0	1
Body-centred cubic (bcc)	$8\times1/8=1$	0	1	2
Face-centred cubic (fcc)	$8\times1/8=1$	$6\times1/2=3$	0	4

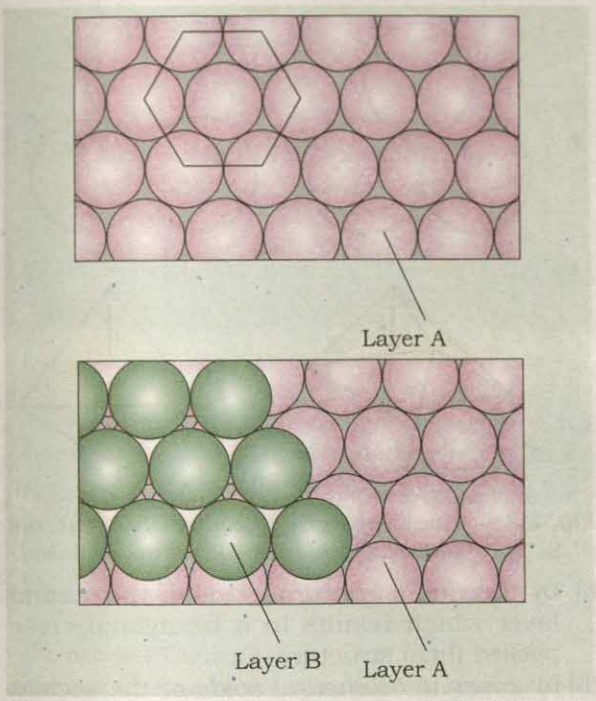


Fig. 2.13 *A close packed structure can be built up in stages. The first layer (A) is laid down with minimum waste of space, and the second layer (B) lies in the depression of the first layer.*

For the third layer, there are two alternatives,

(i) Spheres are placed in the depressions of the second layer which are directly above the spheres of the first layer. In this scheme, the third layer duplicates the first layer A and next layer (fourth) duplicates B and so on. This leads to the layers being stacked in a pattern AB AB AB .... which results in a **hexagonal close packed** (hcp) structure (Fig. 2.14 and 2.15). This sort of arrangement of atoms is found in many metals like magnesium and zinc.

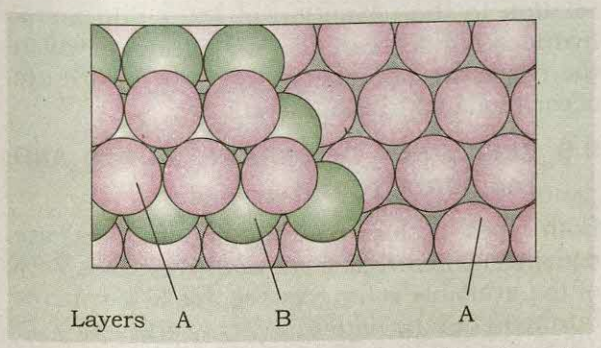


Fig. 2.14 *The third layer of spheres lies above the spheres of the first layer to give an AB AB AB.... structure.*

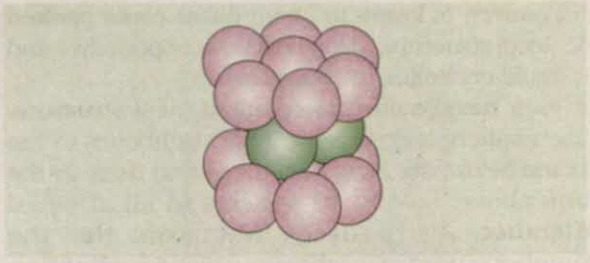


Fig. 2.15 *A fragment of the structure formed, as described in Fig. 2.14, shows the hexagonal symmetry of the arrangement and the origin of its name 'hexagonal close-packed structure'.*

(ii) In the second alternative, the spheres of the third layer lie in the depressions of the second layer that do not lie directly over the atoms of the first layer (Fig. 2.16). If we call this third layer 'C', then the resulting structure has an ABC ABC....

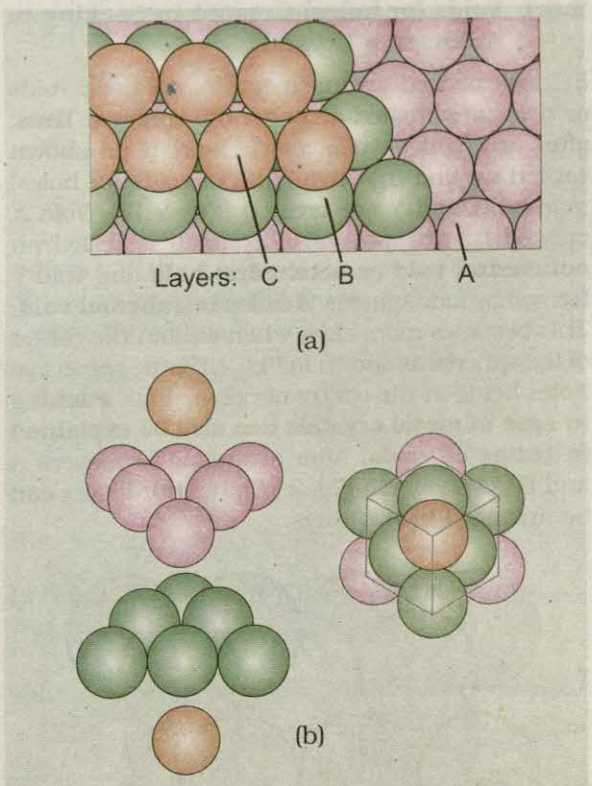


Fig. 2.16 *(a) As an alternative to the scheme shown in Fig. 2.14 the spheres of the third layer can lie above the depressions in the first layer to give an ABC ABC.... arrangement of layers. (b) The fragment of the structure formed, as described in (a) above shows the origin of the names 'cubic close-packed structure' or 'face centerd cubic structure'.*

pattern of layers to give a **cubic close packed** (ccp) structure. Metals such as copper, silver and gold crystallize in this structure.

In a **hexagonal close packed** (hcp) structure, each sphere has three nearest neighbours in the plane below, six in its own plane and three in the one above, having 12 spheres in all at equal distances. Alternatively, this means that the number of nearest neighbours called **coordination number** of each atom in this arrangement of solid is 12. It is impossible to pack identical spheres together with a coordination number greater than 12. The close packed structure adopted by a metal is associated with lowest energy.

In crystals with directional bonds, coordination number is lower compared to crystals with non-directional bonds (as in case of metals and ionic compounds).

2.5.1 Voids (or holes) Created in Packing of Atoms in a Crystal

In close packed arrangements of spheres, voids or holes are created amongst the spheres. Thus, after arranging two layers (A and B as shown earlier) we find that two types of voids (or holes) marked X and Y are created (Fig. 2.17). Void X created by six spheres in contact, is called an **octahedral void** or **octahedral hole** and void Y formed by four spheres is called **tetrahedral void**. This becomes more clear when we join the centre of the spheres as shown in Fig. 2.18, the respective holes being at the centre of polyhedron. **Packing in case of metal crystals can also be explained in terms of voids.** After arranging two layers A and B (as shown in Fig. 2.13), the third layer can be arranged in two ways:

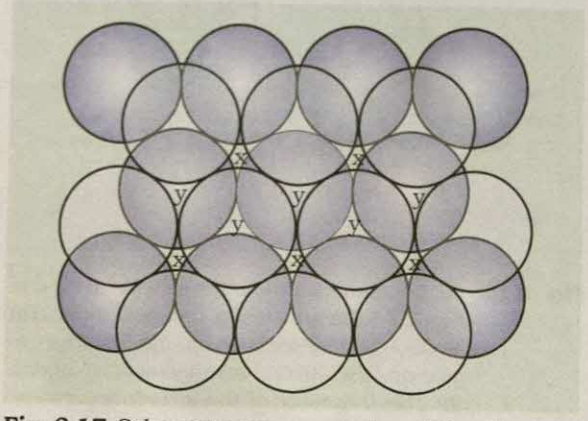


Fig. 2.17 *Schematic representation of the first and second layers of hard spheres. X and Y are octahedral and tetrahedral voids respectively.*

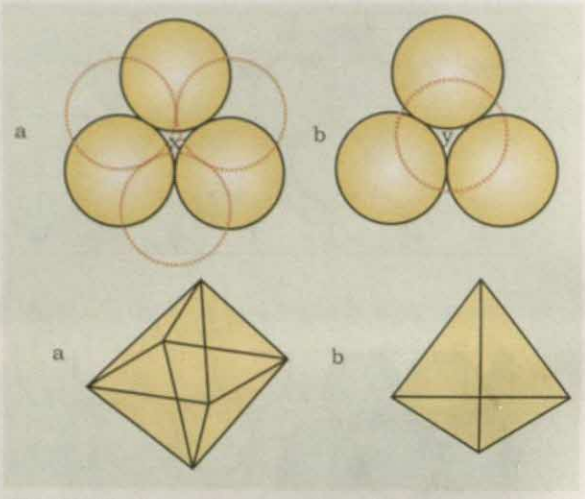


Fig. 2.18 *Two types of voids in crystals (a) Octahedral void, (b) Tetrahedral void.*

(i) by *covering tetrahedral voids* of the second layer which results in a hexagonal close packed (hcp) structure, Or,

(ii) by *covering octahedral voids* of the second layer. If we go on arranging layers, we find that there is one atom below the octahedral void and one atom above it (in this scheme). In this arrangement called cubic close packed (ccp), atoms in the first layer and atoms in the fourth layer are vertically aligned.

In both these arrangements i.e., in hcp and ccp structures, 74% of the total space is occupied by the atoms (spheres) while 26% space remains vacant. In contrast to this, packing in body centred cubic (bcc) structure is not that efficient and only 68% space is occupied by the atoms (spheres).

The voids or holes in crystals are also called **interstices**. Their size acquires importance in relation to the formation of transition metal hydrides, borides, carbides and nitrides in which the respective non-metals (H, B, C and N) are accommodated in the interstices.

2.6 EFFICIENCY OF PACKING IN hcp AND ccp STRUCTURES

Both types of close packing (hcp and ccp) are equally efficient that is, in both the cases 74% of the available volume is occupied by spheres (atoms). Let us calculate the efficiency of packing in ccp structure. In (Fig. 2.19), let the unit cell edge length be 'a' and face diagonal AC = b.

In Δ ABC

$AC^2 = b^2 = BC^2 + AB^2$

$= a^2 + a^2 = 2a^2$

or $b = \sqrt{2}\,a$

If r is the radius of the sphere, we find

$$b = 4r = \sqrt{2}\,a$$

$$\text{or } a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}\,r \qquad (2.2)$$

(we can also write, $r = \frac{a}{2\sqrt{2}}$)

We know, per unit cell in ccp structure, that has effectively 4 spheres and total volume of four spheres is equal to $4 \times (4/3)\pi r^3$ and volume of the cube is a^3 or $(2\sqrt{2}r)^3$ using Eq. (2.2). Therefore,

$$\text{Percentage efficiency} = \frac{\text{Volume occupied by four spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}}\%$$

$$= \frac{4 \times (4/3)\pi r^3 \times 100}{(2\sqrt{2}\,r)^3}\%$$

$$= \frac{(16/3)\pi\, r^3 \times 100}{16\sqrt{2}\, r^3}\% = 74\%$$

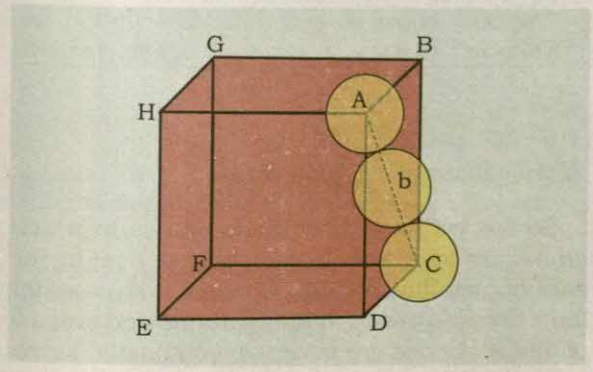


Fig. 2.19 *Cubic close packing–other sides are not provided with spheres for sake of clarity.*

2.6.1 Efficiency of Packing in Body Centred Cubic Structures

From the (Fig. 2.20), it is clear that the atom at the centre will be in touch with other two atoms diagonally arranged.

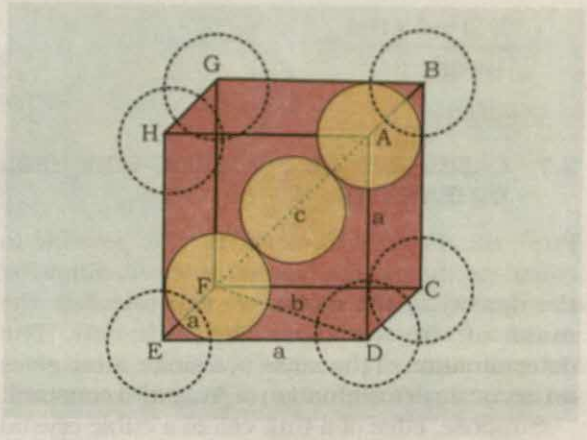


Fig. 2.20 *Body centred cubic unit cell (sphere along the body diagonal are shown with solid boundaries).*

In Δ EFD,

$b^2 = a^2 + a^2 = 2a^2$

$b = \sqrt{2}\,a$

Now in Δ AFD

$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$

$c = \sqrt{3}\,a$

The length of the body diagonal c is equal to 4r, where r is the radius of the sphere (atom).

But c = 4r, as all the three spheres along the diagonal touch each other.

Therefore, $\sqrt{3}\,a = 4r$

$$a = \frac{4r}{\sqrt{3}} \qquad (2.3)$$

Also we can write, $r = \frac{\sqrt{3}}{4}a$ (2.4)

In this sort of structure total number of atoms is two and their volume is $2 \times (4/3)\pi\, r^3$.

Volume of the cube, a^3 will be equal to $(\frac{4}{\sqrt{3}}\,r)^3$ or

$a^3 = (\frac{4}{\sqrt{3}}\,r)^3$. Therefore,

$$\text{Percentage efficiency} = \frac{\text{Volume occupied by two spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}}\%$$

$$= \frac{2 \times (4/3)\pi r^3 \times 100}{\left[(4/\sqrt{3})r\right]^3}\%$$

$$= \frac{(8/3)\pi r^3 \times 100}{\left[64/(3\sqrt{3})\right] r^3}\%$$

$$= 68\%$$

2.7 CALCULATIONS INVOLVING UNIT CELL DIMENSIONS

From the unit cell dimensions, it is possible to calculate the volume of the unit cell. Knowing the density of the metal, we can calculate the mass of the atoms in the unit cell. The determination of the mass of a single atom gives an accurate determination of Avogadro constant.

Suppose, edge of a unit cell of a cubic crystal determined by X-ray diffraction is a, d is density of the solid substance and M is the molar mass, then in case of cubic crystal,

volume of a unit cell = a^3

Mass of the unit cell = number of atoms in the unit cell × mass of each atom

$= z \times m$

(Here z is the number of atoms present in one unit cell and m is the mass of a single atom).

Mass of an atom present in the unit cell,

$$m = \frac{M}{N_A} \quad (M \text{ is molar mass})$$

Therefore, density of the unit cell,

$$d = \frac{\text{mass of unit cell}}{\text{volume of unit cell}} \quad \text{or,}$$

$$d = \frac{z.m}{a^3} = \frac{z.M}{a^3.N_A} \quad \text{or} \quad d = \frac{zM}{a^3 N_A} \qquad (2.5)$$

Remember, the density of the unit cell is the same as the density of the substance. The density of the solid can always be determined by other methods. Out of the five parameters (d, z, M, a and N_A), if four are known, we can determine the fifth.

Example 2.2

An element has a body centred cubic(bcc) structure with a cell-edge of 288 pm. The density of the element is 7.2 g/cm^3. How many atoms are present in 208 g of the element?

Solution

Volume of the unit cell = (2.88 pm)^3

$= (288 \times 10^{-12}\ \text{m})^3 = (288 \times 10^{-10}\ \text{cm})^3$

$= 2.39 \times 10^{-23}\ \text{cm}^3$

Volume of 208 g of the element

$$= \frac{\text{mass}}{\text{density}} = \frac{208\,\text{g}}{7.2\,\text{g cm}^{-3}} = 28.88\,\text{cm}^3$$

Number of unit cells in this volume

$$= \frac{28.88\,\text{cm}^3}{2.39 \times 10^{-23}\,\text{cm}^3/\text{unit cell}}$$

$$= 12.08 \times 10^{23}\ \text{unit cell}$$

Since each bcc cubic unit cell contains 2 atoms, therefore, the total number of atoms in 208 g

$= 2\ (\text{atoms/unit cell}) \times 12.08 \times 10^{23}$ unit cells

$= 24.16 \times 10^{23}$ atoms

Example 2.3

X-ray diffraction studies show that copper crystallizes in an fcc unit cell with cell edge of 3.608×10^{-8} cm. In a separate experiment, copper is determined to have a density of 8.92 g/cm^3, calculate the atomic (molar) mass of the copper.

Solution

In case of fcc lattice, number of atoms per unit cell, z = 4 atoms

Therefore, $M = \dfrac{d\,N_A a^3}{z}$

$$= \frac{8.92\,\text{g cm}^{-3} \times 6.022 \times 10^{23}\,\text{atoms mol}^{-1} (3.608 \times 10^{-8}\,\text{cm})^3}{4\ \text{atoms}}$$

$$= 63.1\,\text{g/mol}$$

Atomic mass of copper = 63.1 u

So far, we have discussed crystals in which atoms are identical. In fact, this is true in the case of metallic crystals. We shall now consider ionic crystals in which ions (cations and anions) of different sizes are to be accommodated in the structure.

2.8 THE STRUCTURE OF IONIC CRYSTALS

In ionic crystals, there are two types of ions – cations and anions, both may have different sizes and charges. Opposite charges attract each other and therefore there is a tendency for ions of one type of charge to group around ions of the opposite charge. Due to difference in ionic

sizes, structure of a given ionic solid is decided by geometrical considerations that arise while stacking ions of different sizes.

We know that positive ions are smaller than their parent atoms. Contrary to this, negative ions are larger than their parent atoms. In an ionic solid, electrical neutrality is always to be maintained. The ionic radius ratios of *cation* and *anion* play a very important role in giving a clue to the nature of the crystal structure of the ionic substance. It follows from geometrical consideration that a coordination number of 8 is expected in an ionic substance of AB type when the radius ratio exceeds 0.732. For a ratio between 0.732 and 0.414, a coordination number of 6 is expected, and coordination number of 4 is likely for a ratio of less than 0.414. This is summarised in the Table 2.4.

This can be understood if we arrange anions around cation and vice versa. Keeping size of the cations same, as the size of the anion decreases, the coordination number increases as can be seen in (Fig. 2.21).

In a ccp structure, if there are N spheres (atoms or ions), there are 2N tetrahedral voids and N octahedral voids. In a face centred cubic (fcc) unit cell there are 4 atoms/ions, therefore, there are 4 octahedral voids and 8 tetrahedral voids. A tetrahedral void can accommodate an ion of radius $r^+ = 0.225\ r^-$ and an octahedral void can accommodate an ion of radius $r^+ = 0.414\ r^-$.

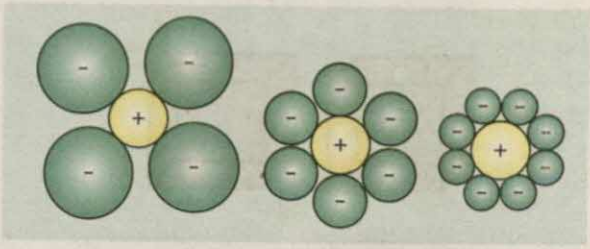


Fig. 2.21 *Illustrating the importance of ionic ratio in packing (As the ratio r^+/r^- increases more number of anions can be arranged around cations).*

2.8.1 Locating Tetrahedral and Octahedral Voids

We know close packed structures have both-octahedral and tetrahedral voids. In a ccp structure, there is 1 octahedral void in the centre of the body and 12 octahedral voids on the 12 edges of the cube. Each octahedral void on the edge is common to four other unit cells (Fig. 2.22). Thus, in cubic close packed structure:

Octahedral voids in the centre of the cube = 1

Effective number of octahedral voids

$$\text{located at the edges} = 12 \times \frac{1}{4} = 3$$

Total number of Octahedral voids = 4

In ccp structure, there are 8 tetrahedral voids. In close packed structure, there are eight spheres in the corner of the unit cell and each sphere is in contact with three others giving rise to eight tetrahedral voids.

Table 2.4 Radius Ratio in 1:1 or AB Type Structure*

Limiting radius ratio (r^+/r^-)	Polyhedron	Structure Type	Coordination number	Examples
0.732 and more	Cube	Caesium chloride	8	CsI, CsBr, TlBr, NH_4Br
0.414 - 0.732	Octahedron	Sodium chloride (rock salt)	6	MgO, NaBr, CaS, MnO, KBr, CaO
0.225 - 0.414	Tetrahedron	Sphalerite, ZnS	4	CuCl, CuBr, CuI, BaS, HgS

* There are exceptions for each type of structures e.g. BeS($r^+/r^- = 0.19$) has sphalerite structure; LiI($r^+/r^- = 0.34$), LiBr($r^+/r^- = 0.38$), KCl ($r^+/r^- = 0.77$), RbCl($r^+/r^- = 0.83$), BaO($r^+/r^- = 0.97$) have sodium chloride or rock salt structure.

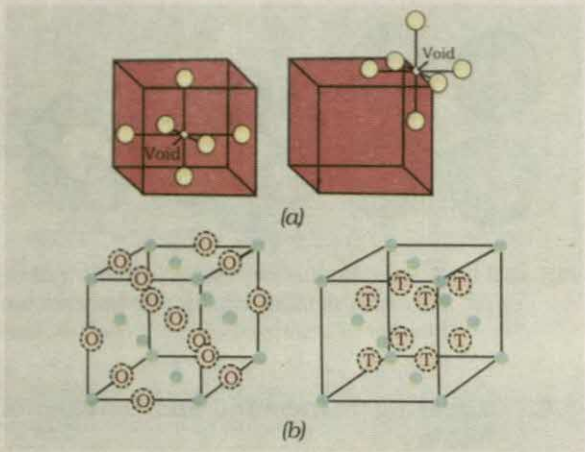


Fig. 2.22 *(a) Octahedral holes (void) in a face-centred cubic lattice*
(b) Octahedral holes are indicated by O and tetrahedral holes are indicated by T.

2.8.2 AB^1 type Structures of Ionic Crystals

1. *Caesium Chloride Structure*: Caesium chloride structure is a body centred cubic structure. Cs^+ ions are large enough to have eight Cl^- ions around them. The Cl^- ions are at the corners of a primitive cubic array. There is a big central empty region in each Cl^- array and Cs^+ ion fits into it. The structure may be considered to be built of two interpenetrating primitive cubic lattices (one of Cs^+ and another of Cl^-). Each Cs^+ ion is surrounded by eight Cl^- ions, and vice versa and so the structure has 8:8 coordination (Fig. 2.23).

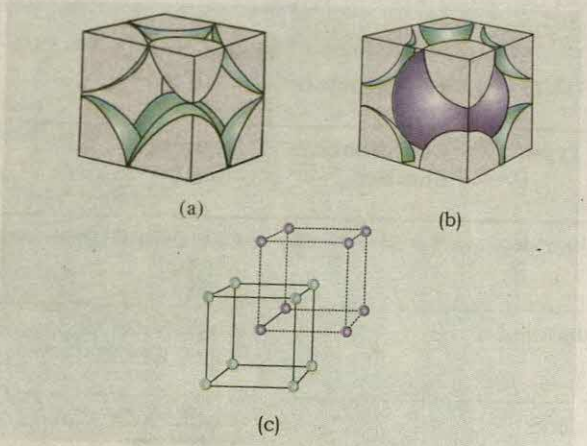


Fig. 2.23 *The caesium chloride structure*
(a) Primitive cubic Cl^- array
(b) a Cs^+ ion enters the void
(c) the resulting primitive cubic arrays.

[1] *A represents cation and B represents anion.*

2. *Sodium Chloride Structure (Rock Salt Structure)*: NaCl has face centred cubic (fcc) structure. Imagine a fcc lattice formed by Na^+ ions and another fcc lattice formed by Cl^- ions. When two lattices are interpenetrated half-way through, the resulting structure represents the structure of NaCl. In complete structure, each Na^+ is surrounded by 6 Cl^- ions and vice versa. In this octahedral arrangement, coordination number of both Na^+ and Cl^- is 6 (Fig. 2.24).

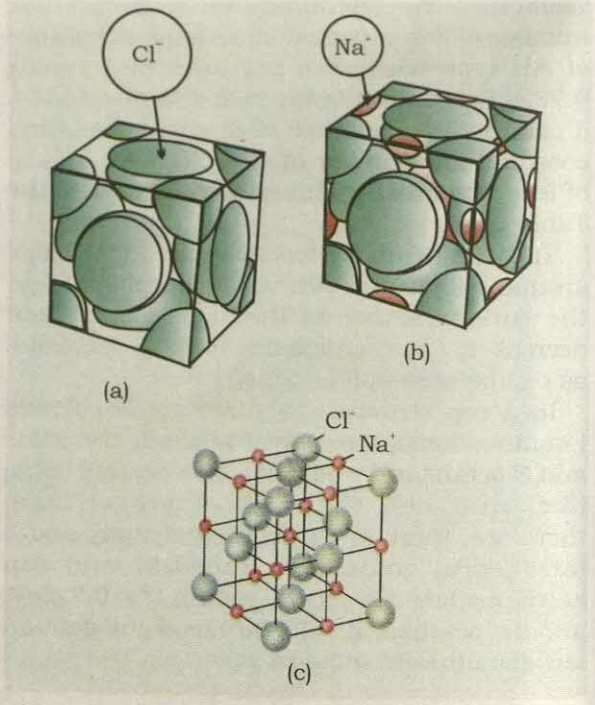


Fig. 2.24 *The sodium chloride structure*
(a) the fcc Cl^- ions array
(b) the Na^+ ions enter the voids
(c) the resulting two interpenetrating fcc arrays.

3. The *Sphalerite (ZnS) structure*: ZnS has face centred cubic lattice in which a Zn^{2+} ion is surrounded by four S^{2-} ions and vice versa. Here, if the sulphide ions are placed at the lattice points, there are zinc ions at one fourth of the distance along each body diagonal. One unit cell of ZnS consists of four Zn^{2+} and four S^{2-} ions making 4 ZnS formula units (Fig. 2.25). [Here electronegativity difference between Zn and S is very small i.e., only 0.9 (electronegativity for Zn = 1.6 and S = 2.5), therefore, the bond between Zn and S has significant covalent character.

Fig. 2.25 (b) gives structure of diamond and it can be seen that it is similar to that of sphalerite.

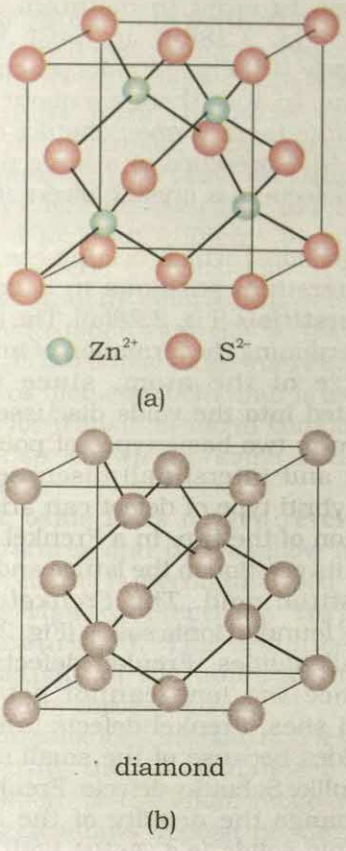


Fig. 2.25 *(a) ZnS structure (b) Diamond structure. Both structures are identical.*

2.8.3 Ionic Structures Based on Close Packing of Anions

Many ionic crystal structures can be described as close-packed arrangements of the large anions with the smaller cations occupying the voids in the arrangement. Let us consider sodium chloride (NaCl) and sphalerite (ZnS) structures. Here both have structures based on *face centred cubic lattice.* If the anions are large enough to touch each other, they have a cubic close packed arrangement. For sodium chloride, Cl^- ions form fcc lattice and sodium ions, Na^+ go into all octahedral voids (Fig. 2.24). Similarly, in ZnS (sphalerite), S^{2-} ions form fcc lattice and Zn^{2+} ions go into alternate tetrahedral voids. In a fcc unit cell, there are eight tetrahedral voids. Thus, there are four Zn^{2+} ions and four S^{2-} ions giving 4 ZnS units per unit cell.

2.8.4 AB_2 and A_2B Type Structures

The next simplest types of ionic crystal structures are the 1:2 and 2:1 type popularly known as AB_2 type and A_2B type structures, respectively. Calcium fluoride (fluorite), CaF_2 is an example of AB_2 type compounds (Fig. 2.26). Other ionic structures similar to CaF_2 structure are grouped under *fluorite structure.* The calcium ions, Ca^{2+} are located at the face centred cubic lattice points and, therefore, have cubic closed-packed arrangement. The fluoride ions (F^- ions) occupy all the eight tetrahedral voids. Thus, there are four Ca^{2+} ions and eight F^- ions in the unit cell of calcium fluoride. Other ionic compounds that have the fluorite structure include SrF_2, BaF_2, PbF_2 and $BaCl_2$.

Several A_2B type compounds have structures reverse to the fluorite structure;

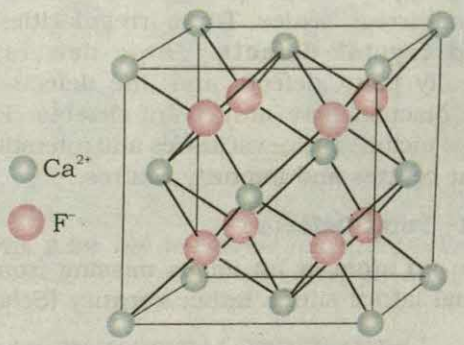


Fig. 2.26 *CaF_2 Structure.*

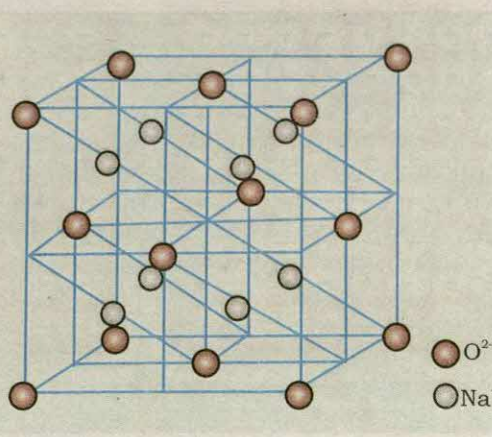


Fig. 2.27 *Na_2O Structure:an example of antifluorite structure.*

hence the so called *antifluorite structure*. In the antifluorite structure the position of cations and anions as obtained in the fluorite structure gets reversed. In this structure, the smaller cations occupy the positions of fluoride ions, and the larger anions occupy the positions of the calcium ions in the fluorite structure. For example in Na_2O, oxide ions (O^{2-}) have a cubic close packed arrangement and Na^+ ions occupy all the tetrahedral voids (Fig. 2.27). There are several oxides and sulphides which have antifluorite structure such as Li_2O, K_2O, Rb_2O and Rb_2S.

2.9 IMPERFECTION IN SOLIDS

In actual practice it is difficult to grow a perfect crystal. A real solid commonly consists of a matrix of many small individual crystals or grains, each of which is deformed because it is highly packed among other deformed grains. Even *single crystals* grown with all care and which appear to be perfect, contain many internal irregularities. These irregularities are called **crystal defects**. These defects are basically point defects and line defects. We shall discuss here only point defects. Point defects include lattice vacancies and interstitials, colour centres and impurity centres.

2.9.1 Point Defects

When an atom or an ion is missing from its normal lattice site, a lattice vacancy (*Schottky defect*) is created. In stoichiometric ionic crystals, a vacancy of one ion has to be accompanied by the vacancy of the oppositely charged ion in order to maintain electrical neutrality [Fig. 2.28(b)]. In NaCl, there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In $1cm^3$ there are about 10^{22} ions and, therefore there is one Schottky defect per 10^{16} ions. The presence of a large number of Schottky defects in a crystal lowers its density markedly.

Atoms (or ions) which occupy the normally vacant interstitial positions in a crystal are called **interstitials** [Fig. 2.28(a)]. The important factor determining the formation of interstitials is the size of the atom, since they are accomodated into the voids discussed earlier. In addition to two basic types of point defects (Schottky and interstitial) discussed above, another hybrid type of defect can arise from a combination of the two. In a Frenkel defect an ion leaves its position in the lattice and occupies an interstitial void. The *Frenkel defect* is commonly found in ionic solids [Fig. 2.28(c)]. In pure alkali halides, Frenkel defects are not found since the ions cannot get into the interstitial sites. Frenkel defects are found in silver halides because of the small size of the Ag^+ ion. Unlike Schottky defects, Frenkel defects do not change the density of the solids. In certain ionic solids (e.g. AgBr) both Schottky and Frenkel defects occur.

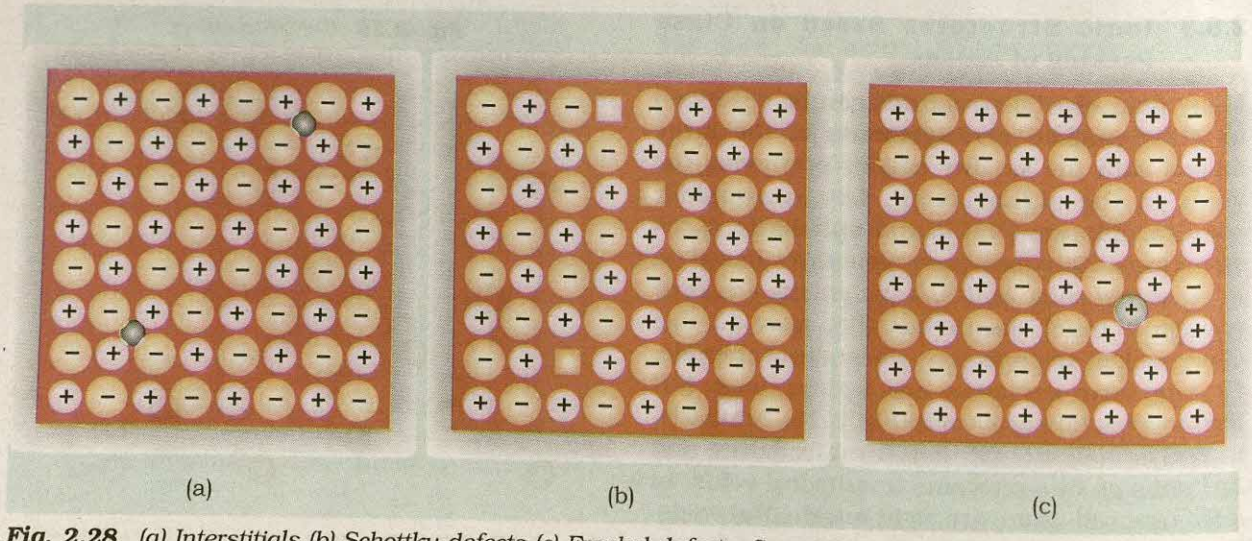


Fig. 2.28 *(a) Interstitials (b) Schottky defects (c) Frenkel defects. Squares represent vacancies and darkened circles represent interstitials.*

2.9.2 Non-Stoichiometric Point Defects

The defects discussed above do not disturb the stoichiometry of the crystalline material. There is large variety of non-stoichiometric inorganic solids which contain an excess or deficiency of one of the elements. Such solids showing deviations from the ideal stoichiometric composition form an important group of solids. For example in the vanadium oxide, VO_x, x can be anywhere between 0.6 and 1.3. There are solids which are difficult to prepare in the stoichiometric composition. Thus, the ideal composition in compounds such as FeO is difficult to obtain (normally we get a composition of $Fe_{0.95}O$ but it may range from $Fe_{0.93}O$ to $Fe_{0.96}O$). Non-stoichiometric behaviour is most commonly found for transition metal compounds though it is also known for some lanthanoids and actinoids.

Zinc oxide loses oxygen reversibly at high temperatures and turns yellow in colour. The excess metal is accommodated interstitially, giving rise to electrons trapped in the neighbourhood. The enhanced electrical conductivity of the non-stoichiometric ZnO arises from these electrons.

Anion vacancies in alkali halides are produced by heating the alkali halide crystals in an atmosphere of the alkali metal vapour. When the metal atoms deposit on the surface they diffuse into the crystal and after ionisation the alkali metal ion occupies cationic vacancy whereas electron occupies anionic vacancy. Electrons trapped in anion vacancies are referred to as **F-centres** (from *farbe* the German word for colour) that gives rise to interesting colour in alkali halides [Fig. 2.29(a)]. Thus, the excess of potassium in KCl makes the crystal appear violet and the excess of lithium in LiCl makes it pink.

Another common method of introducing defects in ionic solids is by adding impurity ions having different charge than host ions. Literature abounds in examples where interstitials or vacancies are produced by addition of impurities to ionic solids. For example, addition of $CdCl_2$ to AgCl (or of $SrCl_2$ to NaCl) yields solid solutions where the divalent cation Cd^{2+} (or Sr^{2+}) occupies the Ag^+ (or Na^+) sites and produces cation vacancies equal in number to that of the divalent ions [Fig. 2.29(b)].

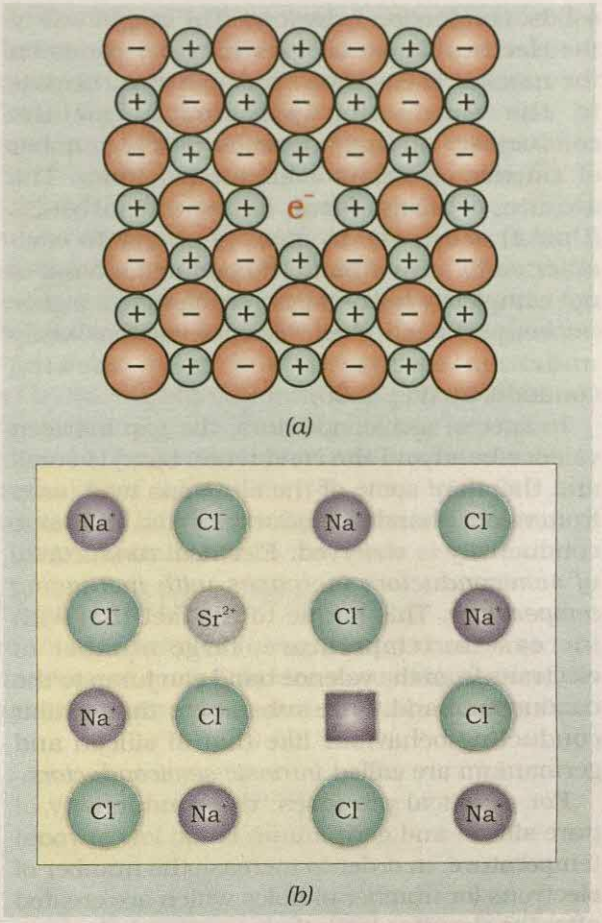


Fig. 2.29 *(a) An F-center in a crystal (b) Introduction of cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}.*

2.10 ELECTRICAL PROPERTIES

Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude; probably no other physical property experiences this range of variation. In fact, one way of classifying solid materials is according to the ease with which they conduct electricity. Accordingly, solids are classified in three groups: conductors, semiconductors and insulators. Metals are good **conductors** and have conductivities in the order 10^7 $(\Omega m)^{-1}$. At the other extreme are solids with very low conductivities, ranging between 10^{-10} and 10^{-20} $(\Omega m)^{-1}$, these are electrical **insulators**. The solids with intermediate conductivities generally from 10^{-6} to 10^4 $(\Omega m)^{-1}$ are termed **semiconductors** (Unit 5).

In most of the solids and many insulating solids, conduction is through electron movement under an electric field. However, in some ionic

solids, conduction is by ions. The magnitude of the electrical conductivity strongly depends on the number of electrons available to participate in the conduction process. In metals, conductivity strongly depends on the number of valence electrons available per atom. The atomic orbitals form molecular orbitals (Unit 1) which are so close in energy to each other as to form a **band**. If conduction band is not completely full or it lies very close to a higher unoccupied band, then electrons can flow easily under an electric field thereby showing conductivity (Fig. 2.30).

In case of semiconductors, the gap between valence band and the conduction band is small and therefore some of the electrons may jump from valence band to conduction band and some conductivity is observed. *Electrical conductivity of semiconductors increases with increasing temperature.* This is due to the fact that with increase in temperature, large number of electrons from the valence band can jump to the conduction band. Pure substances that exhibit conducting behaviour like that of silicon and germanium are called *intrinsic semiconductors.*

For practical purposes, the conductivity of pure silicon and germanium is too low at room temperature. In order to increase the number of electrons (or number of holes which are created after the electrons leave their positions), the pure substances are carefully *doped* with impurities. Doping means introduction of small amount of impurities like phosphorous, arsenic or boron into the pure crystal. Conductivity of silicon increases dramatically by doping it with certain other elements. In pure crystalline silicon at room temperature, four valence electrons of each atom are used for forming four normal covalent bonds with four adjacent Si atoms. When a silicon crystal is doped with a group-15 element, such as P, As, Sb or Bi, the structure of the crystal lattice is left unchanged, but an occasional atom with five valence electrons occupies a site that would normally be occupied by a silicon atom. The foreign atom (i.e., dopant) uses four of its electrons in covalent bonding just as if it were a silicon atom, but because the fifth electron is not needed for bonding it becomes delocalised and is thus free to contribute to electrical conduction. Silicon that has been doped with a group-15 element is called an *n-type semiconductor*, '*n*' standing for negative since electrons are responsible for the semiconducting behaviour (Fig. 2.31). Doping a silicon crystal with a group-13 element, such as B, Al, Ga or In produces a silicon crystal structure in which an occasional dopant atom is present with only three valence electrons. The place where the fourth valence electron is missing is called an **electron vacancy** or a **hole**. Such holes can move through the

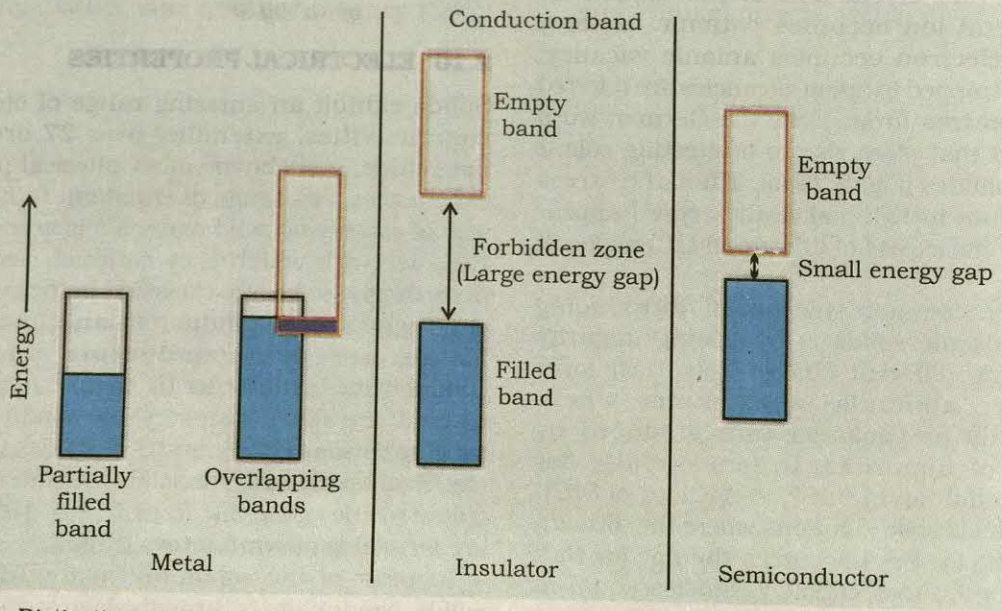


Fig. 2.30 *Distinction among metals, insulators and semiconductors. In each case, an unshaded area represents a conduction band.*

crystal like a positive charge giving rise to electrical conductivity. Direction of motion of the holes in an electric field is opposite to that of the electrons. Group-13 doped crystals of silicon are called a *p-type semiconductors* since holes (positive in charge) appear to be responsible for the semiconducting properties. *n*-type and *p*-type semiconductors are shown in (Fig. 2.32). Various combinations of *n*-type and *p*-type semiconductors are used to make electronic components, for example a *diode* is a combination of *p*- and *n*-type semiconductors and is used as a rectifier. *Transistors* which are *pnp* or *npn* 'sandwich' semiconductor are used to detect or amplify radio or audio signals. The *solar cell* is essentially an efficient photo diode used for converting radiant (light) energy into electrical energy.

Germanium and silicon are group-14 elements and have, therefore, a characteristic valence of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combination of elements of group-13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si. Typical of group 13–15 compounds are InSb, AlP and GaAs. Gallium arsenide(GaAs) semiconductors have very fast responses and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are examples of group 12–16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO_2 and ReO_3 behave like metals. Rhenium oxide, ReO_3 is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO_2, VO_3, TiO_3 show metallic or insulating properties depending on temperature.

2.11 MAGNETIC PROPERTIES

The macroscopic (observable) magnetic properties of materials are a consequence of **magnetic moments** associated with individual

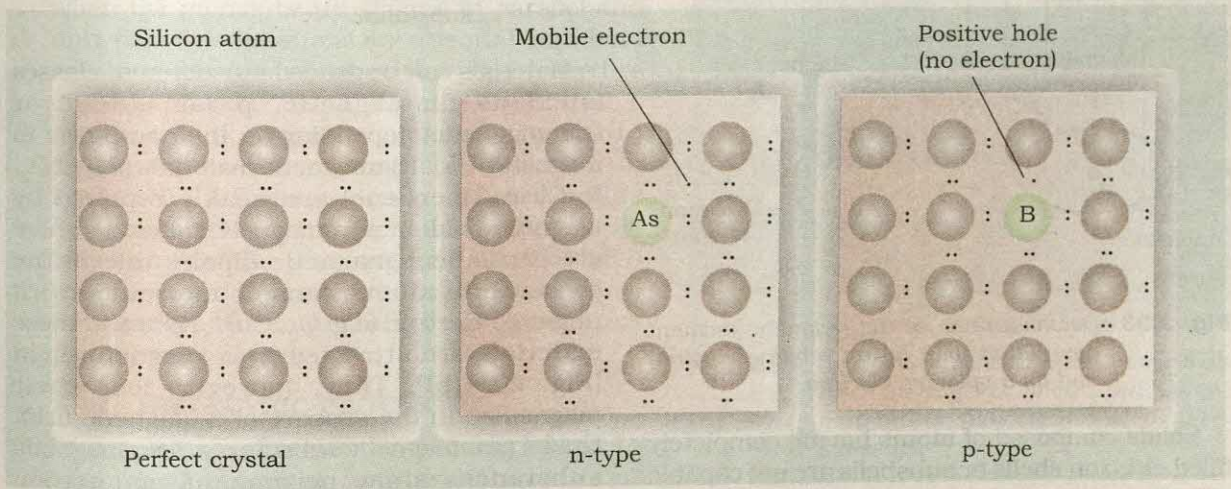


Fig. 2.31 *Creation of n-type and p-type semiconductors by doping groups 13 and 15 elements.*

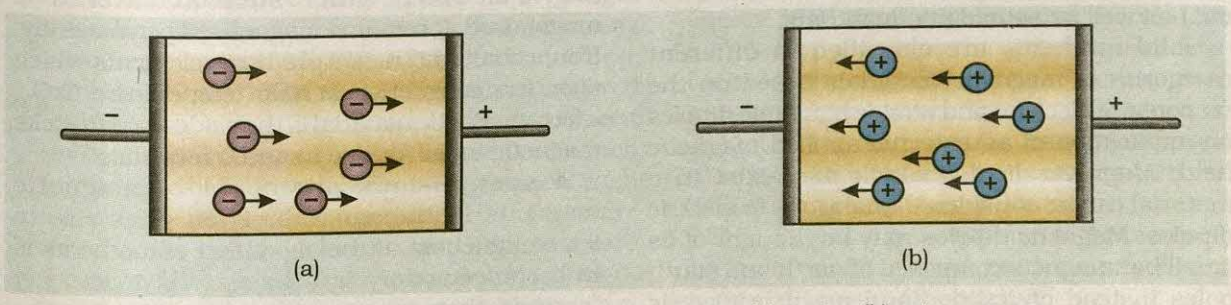


Fig. 2.32 *Conduction in semiconductors: (a) n-type (b) p-type.*

electrons. Each electron in an atom has magnetic moment that originates from two sources. The first one is related to its orbital motion around the nucleus, and the second, to spin of electron around its own axis. A moving electron may be considered to be a small current loop, generating a small magnetic field, and having a magnetic moment along its axis of rotation as shown in [Fig. 2.33(a)]. The other type of magnetic moment originates from electron spin which is directed along the spin axis. Spin magnetic moments are shown in an 'up' or 'down' direction [Fig. 2.33(b)]. Thus, each electron in an atom may be thought of as being a small magnet having permanent orbital and spin magnetic moments. The fundamental magnetic moment is the **Bohr Magneton**, μ_B that is equal to 9.27×10^{-24} A m^2. For each electron in an atom, the spin magnetic moment is $\pm\mu_B$ (depending on the two possibilities of the spin). The contribution of the orbital magnetic moment is equal to $m_l\mu_B$ where m_l is the *magnetic quantum number* of the electron.

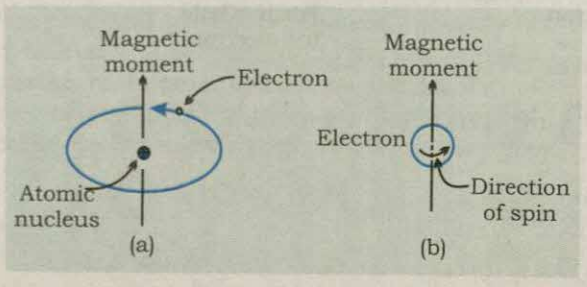


Fig. 2.33 *Demonstration of the magnetic moment associated with (a) an orbiting electron and (b) a spinning electron.*

Solids composed of atoms having completely filled electron shells or subshells are not capable of being permanently magnetised. This category includes the noble gases (such as He, Ne, Ar, etc.) as well as some ionic materials.

Solid materials are classified in different categories of magnetic materials based on the response of electron and atomic magnetic dipoles on application of an external applied magnetic field. *Magnetic dipoles* which may exist in a material can be considered analogous to electric dipoles. Magnetic dipoles may be thought of as small bar magnets composed of north and south poles instead of positive and negative electric charges. In our present discussion, magnetic dipole moment will be represented by arrows [Fig. 2.34(a)].

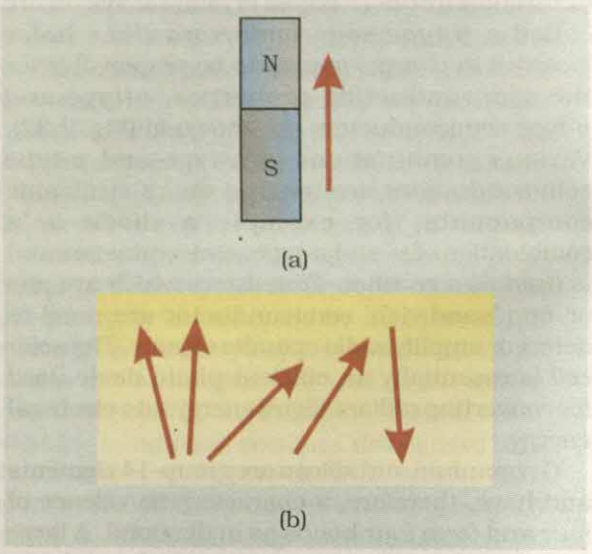


Fig. 2.34 *(a) Magnetic moment as designated by an arrow.*
(b) Magnetic moment in a paramagnetic substance.

Materials can be divided into different classes (such as diamagnetic, paramagnetic or ferromagnetic) depending on their response to magnetic field. Diamagnetic materials (e.g. TiO_2, NaCl and benzene) are weakly repelled by magnetic field. In paramagnetic materials there are permanent magnetic dipoles due to the presence of atoms, ions or molecules with unpaired electron (e.g. O_2, Cu^{2+}, Fe^{3+}) and these materials are attracted by a magnetic field [Fig. 2.34(b)]. They, however, lose their magnetism in the absence of a magnetic field. Unlike paramagnetic substances, ferromagnetic substances show permanent magnetism even when the magnetic field is removed (e.g. Fe, CrO_2). Once such a material is magnetised, it remains magnetised permanently. Iron, cobalt and nickel are three elements which show ferromagnetism at room temperature. CrO_2, a ferromagnetic material is the oxide used to make magnetic tapes for use in audio recording.

A spontaneous alignment of magnetic moments in the same direction gives rise to ferromagnetism. If the alignment of moments is in a compensatory way so as to give zero net moment, then we get antiferromagnetism in the

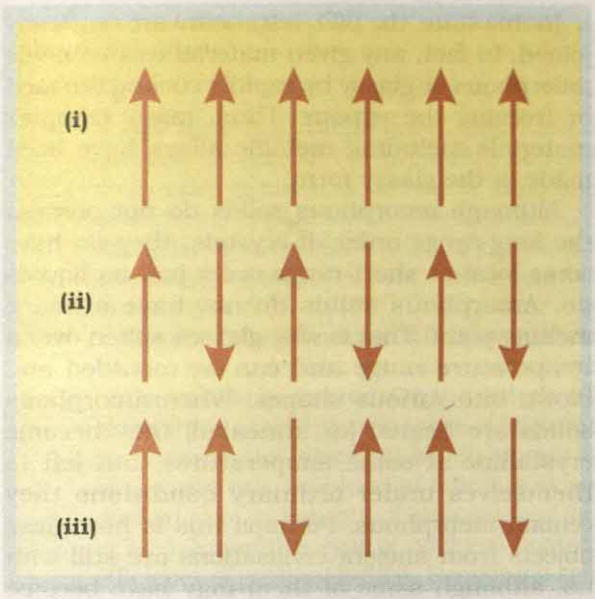


Fig. 2.35 *Schematic alignment of magnetic moments in (i) Ferromagnetic (ii) antiferromagnetic and (iii) Ferrimagnetic.*

material (e.g. MnO). Ferrimagnetism is found when the moments are aligned in parallel and anti-parallel directions in unequal numbers resulting in a net moment (e.g. Fe_3O_4; ferrites of the formula $M^{2+}Fe_2O_4$; M = Mg, Cu, Zn, etc.). Alignment of magnetic moments in ferro-, antiferro- and ferri-magnets is shown in Fig. 2.35. All magnetically ordered solids (ferromagnetic and antiferromagnetic solids) transform to the paramagnetic state at high temperature due to the randomisation of spins. Ferrimagnetic material, Fe_3O_4 becomes paramagnetic at 850 K.

2.12 DIELECTRIC PROPERTIES

In insulators, electrons are closely bound to individual atoms or ions and they do not generally migrate under an applied electric field. However, dipoles are created by a shift in charges resulting in polarization. Besides that there may also be permanent dipoles in the crystal. These dipoles (i) may align themselves in an ordered manner such that there is a net dipole moment in the crystal or (ii) may align themselves in such a manner that dipole moments may cancel each other and (iii) it is also possible that there are no dipoles in the crystals, but only ions are present. The crystals where situation (i) is found, exhibit **piezoelectricity** or **pressure electricity**.

When, such a crystal is deformed by mechanical stress electricity is produced due to displacement of ion or if an electric field is applied to the crystal, there will be atomic displacement causing mechanical strain. The piezoelectric effect is demonstrated in [Fig. 2.36(a,b)].

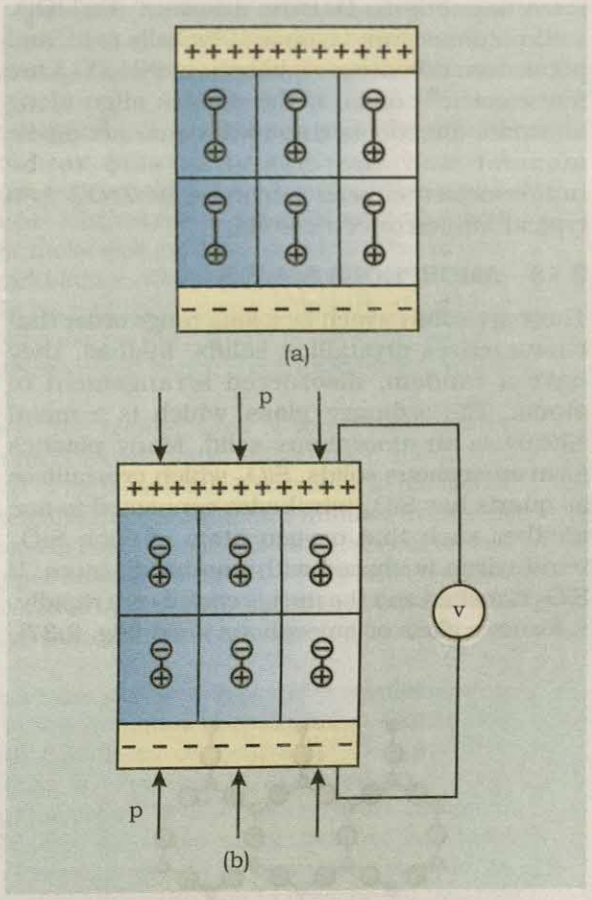


Fig. 2.36 *(a) Dipoles within a piezoelectric material (b) A voltage is generated when the material is subjected to a compressive stress (p).*

Piezoelectric crystals are utilised in transducers, devices that convert electrical energy into mechanical strains, or vice versa. Familiar applications that employ piezoelectrics include phonograph pickups, microphones, ultrasonic generators, strain gauges and sonar detectors. Piezoelectric materials include titanates of barium and lead, lead zirconate ($PbZrO_3$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and quartz. Some of the piezoelectric crystals, when heated produce small electric potential or **pyroelectricity**.

In some of the piezoelectric crystals, the dipoles are permanently lined up (spontaneously polarized) even in the absence of an electric field and the direction of polarisation can be changed by applying an electric field. The phenomenon is called **ferroelectricity** by analogy with ferromagnetism. Barium titanate ($BaTiO_3$), sodium potassium tartarate (Rochelle salt), and potassium dihydrogen phosphate (KH_2PO_4) are ferroelectric[2] solids. If the dipoles align along alternate directions, there will be no net dipole moment and the crystal is said to be *antiferroelectric*. Lead zirconate ($PbZrO_3$) is a typical antiferroelectric solid.

2.13 AMORPHOUS SOLIDS

There are solids which lack long range order that characterises crystalline solids. Instead, they have a random, disordered arrangement of atoms. The ordinary 'glass' which is a metal silicate is an amorphous solid. Many plastics form amorphous solids. SiO_2 which crystallises as quartz has SiO_4 tetrahedra connected to one another such that oxygen atom of each SiO_4 tetrahedron is shared with another Si atom. If SiO_2 is melted and the melt is cooled very rapidly, it forms a glass or amorphous solid (Fig. 2.37).

In this state, the SiO_4 tetrahedra are randomly joined. In fact, any given material can be made amorphous or glassy by rapidly cooling the melt or freezing the vapour. Thus, many complex materials including metallic alloys have been made in the glassy form.

Although amorphous solids do not possess the long-range order of crystals, they do have some local or short-range order just as liquids do. Amorphous solids do not have a sharp melting point. That is why glasses soften over a temperature range and can be moulded and blown into various shapes. When amorphous solids are heated (or annealed) they become crystalline at some temperatures, but left to themselves under ordinary conditions they remain amorphous. Perhaps this is how glass objects from ancient civilisations are still with us, although some of them may have become milky in appearance (instead of being transparent) because of some crystallisation.

Amorphous solids find many applications because of their unique properties. Inorganic glasses are used in construction, houseware, laboratory-ware, etc. Amorphous silicon is likely to be useful material for converting sunlight into electricity (photovoltaic cell).

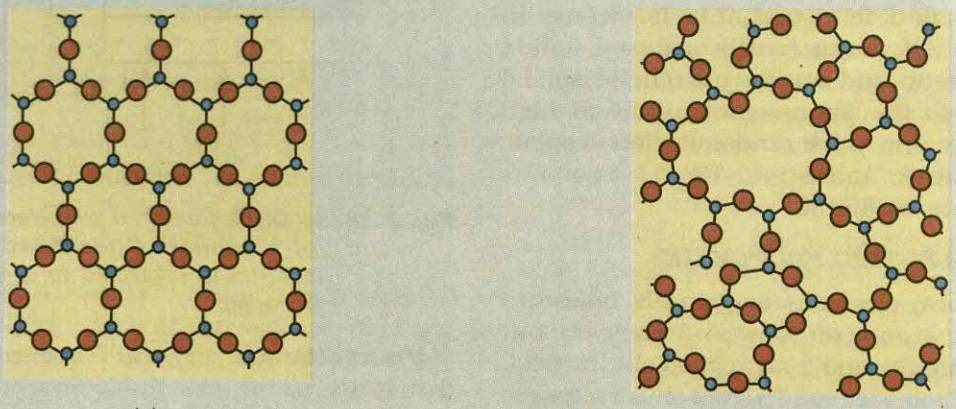


Fig. 2.37 *Two-Dimensional Representation of structures of Crystalline SiO_2 and Amorphous SiO_2*
(a) In crystalline SiO_2, the SiO_4, tetrahedra have a regular arrangement.
(b) In amorphous SiO_2 (silica glass), the SiO_4 tetrahedra have an irregular, random arrangement.

[2] *All ferroelectric solid materials are piezoelectric but the reverse is not true.*

SUMMARY

Solids have long range order, and have definite bonding and structure. Structure and bonding determine the properties of solids. Based on bonding, solids are classified as molecular, covalent or network, ionic and metallic. Structures of crystalline solids are determined experimentally by means of X-ray diffraction, in which the pattern of X-rays diffracted by a crystal is used to calculate the location of atoms/ions in the crystal lattice. The Bragg equation, $n\lambda=2d\sin\theta$ is used to calculate the spacing between various planes in the crystal.

Crystal lattices exhibit different geometries. The *unit cell*, a small portion of the crystal lattice, has a definite geometry and shape and by repeating this unit, the entire crystal lattice can be generated. On the criteria of angles between different edges and edge length along three axes, fourteen types of lattices (Bravais lattices) are obtained. There are several *primitive crystal lattices* in which atoms, ions or molecules are located only in the corners of the unit cell. One kind of lattice is *close-packed lattice*, which can be either *cubic close-packed (ccp)* or *hexagonal close-packed (hcp)*. In each of these cases, efficiency of packing is 74%. In another type of packing, *body centred cubic packing*, which is not close packed, efficiency of packing is 68%. Remaining space in the crystal lattice is occupied by *octahedral voids* and *tetrahedral voids*.

Ionic solids consist of cations and anions at the regular sites of the crystal lattice. Packing in case of these solids depends on the ratio of cation and anion radii (i.e. on r^+/r). Ionic solids are less closely packed as compared to metallic solids. *Coordination number* of an atom or ion is the number of its nearest neighbours. Coordination number in case of closely-packed metal crystals goes to 12, whereas in case of ionic solids, it does not exceed 8. In case of ionic solids, there are different types of structures. AB, AB_2 or A_2B type are commonly known. AB type structures are represented by rock salt (NaCl), caesium chloride and sphalerite (ZnS) whereas AB_2 and A_2B type structures are represented by CaF_2 and Na_2O respectively.

Solids are not perfect in structure and there are different types of imperfections in them. Point defects, line defects are some of the common imperfections. Sometimes point-defects are also created by doping with calculated concentration of impurities. This changes the property of solids and that is exploited in electronic industry. Properties of solids like magnetic, electrical, piezoelectric and ferroelectric are exploited in electronic, audio and other recording devices. All these properties are basically linked with electrons and their movement. Paramagnetic behaviour, for example, is due to presence of unpaired electrons. Enhanced conductivity due to presence of arsenic in silicon is due to free or unbonded electrons in the crystal lattice.

EXERCISES

2.1 Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous.

(a) Tetra phosphorous decoxide (P_4O_{10})
(b) Graphite
(c) Brass
(d) Ammonium phosphate $(NH_4)_3PO_4$
(e) SiC
(f) Rb
(g) I_2
(h) LiBr
(i) P_4
(j) Si
(k) Plastic.

2.2 (a) What is meant by the term '*coordination number*'?

(b) What is the coordination number of atoms

(i) in a cubic close packed structure
(ii) in a body centreed cubic structure.

2.3 How can you determine the atomic mass of an unknown metal if you know its density and the dimension of its unit cell? Explain your answer.

2.4 'Stability of a crystal is reflected in the magnitude of its melting point'. Comment. Collect melting point of water, ethyl alcohol, diethyl ether, and methane from a data book. What can you say about the intermolecular forces between these molecules.

2.5 How will you distinguish between the following pairs of terms:
(a) Hexagonal close packing and cubic close packing.
(b) Crystal lattice and unit cell
(c) Tetrahedral void and octahedral void

2.6 How many lattice points are there in one unit cell of each of the following lattice?
(a) face centred cubic (b) face centred tetragonal (c) body centred cubic.

2.7 Explain:
(a) The basis of similarities and differences between metallic and ionic crystals.
(b) Unit cell is not simply a cube of four sodium ions and four chloride ions.
(c) Can a cube consisting of Na^+ and Cl^- ions at alternate corners serve as a satisfactory unit cell for the sodium chloride lattice?
(d) Ionic solids are hard and brittle.

2.8 Calculate the efficiency of packing in case of a metal crystal for
(a) simple cubic (b) body centred cubic (c) face centred cubic (with the assumption that atoms are touching each other).

2.9 Silver crystallises in fcc lattice. If edge length of the cell is 4.077×10^{-8} cm and density is 10.5 g cm^{-3}, calculate the atomic mass of silver.

2.10 A cubic solid is made of two elements P and Q. Atoms Q are at the corners of the cube and P at the body center. What is the formula of the compound? What are the coordination numbers of P and Q?

2.11 Niobium crystallizes in body centred cubic structure. If density is 8.55 g cm^{-3}, calculate atomic radius of niobium using its atomic mass from the table given earlier in Class XI.

2.12 If the radius of the octahedral void is r and radius of the atoms in close packing is R, derive relation between r and R.

2.13 Copper crystallises into a fcc lattice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3}.

2.14 Formula mass of NaCl is 58.45 g mol^{-1} and density of its pure form is 2.167 g cm^{-3}. The average distance between adjacent sodium and chloride ions in the crystal is 2.814×10^{-8} cm. Calculate Avogadro constant.

2.15 Analysis shows that nickel oxide has formula $Ni_{0.98}O_{1.00}$. What fractions of the nickel exist as Ni^{2+} and Ni^{3+} ions?

2.16 The compound CuCl has ZnS structure. Its density is 3.4 g cm^{-3}. What is the length of the edge of the unit cell?

2.17 If the radius of the bromide ion is 0.182 nm, how large a cation can fit in each of the tetrahedral hole?

2.18 The first order diffraction of X-rays from a certain set of crystal planes occurs at an angle of 11.8° from the planes. If the planes are 0.281 nm apart, what is the wavelength of X-rays?

2.19 What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanisms.

2.20 Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2:1. Can you account for the fact that this substance is a *p*-type semiconductor?

2.21 Ferric oxide crystallises in a hexagonal close packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

2.22 Classify each of the following as being either a *p*-type or an *n*-type semiconductor:
(i) Ge doped with In (ii) B doped with Si

2.23 Thallium chloride, TlCl crystallises in either a simple cubic lattice or a face centreed cubic lattice of Cl^- ions with Tl^+ ions in the holes. If the density of the solid is 9.00 g cm^{-3} and edge of the unit cell is 3.85×10^{-8} cm, what is the unit cell geometry?

2.24 Gold (atomic radius = 0.144 nm) crystallises in a face centreed unit cell. What is the length of a side of the cell?

2.25 In terms of band theory, what is the difference (i) between a conductor and an insulator (ii) between a conductor and a semiconductor?

2.26 Explain the following terms with suitable examples:
(i) Schottky defect (ii) Frenkel defect (iii) Interstitials (iv) F-centres

2.27 The ions of NaF and MgO all have the same number of electrons, and the internuclear distances are about the same (235 pm and 215 pm). Why then are the melting points of NaF and MgO so different (992° C and 2642° C)?

2.28 Explain the term *ionic radius ratio* and its significance in case of ionic crystals. Calculate the ratio for the alkali metal bromides on the basis of the data given below and predict the form of the crystal structure in each case.
ionic radius (in pm)

Li^+	= 74	Rb^+	= 14
Na^+	= 102	Cs^+	= 170
K^+	= 138	Br^-	= 195

2.29 Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.
(a) What is the length of the side of the unit cell?
(b) How many unit cells are there in 1.00 cm^3 of aluminium?

2.30 If NaCl is doped with 10^{-3} mol % of $SrCl_2$, what is the concentration of cation vacancies?

2.31 KF has NaCl structure. What is the distance between K^+ and F^- in KF, if the density is 2.48 g cm^{-3}?

2.32 Calculate the value of the Avogadro constant from the following data:
Density of NaCl = 2.165 g cm^{-3}
Distance between Na^+ and Cl^- in NaCl = 281 pm

2.33 Explain the following with suitable examples:
(a) ferromagnetism (d) piezoelectric effect
(b) paramagnetism (e) antifluorite structure
(c) ferrimagnetism (f) 12-16 and 13-15 group compounds

2.34 Define the term 'amorphous'. Give a few examples of amorphous solids.

2.35 What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass?

UNIT 3

SOLUTIONS

OBJECTIVES

After studying this Unit, you will be able to:

- express concentration of solution in different units.
- state and explain Henry's law and Raoult's law.
- distinguish between ideal and nonideal solutions.
- explain deviations of real solutions from Raoult's law.
- describe colligative properties of solutions and correlate these with molecular masses of the solutes.
- explain abnormal colligative properties exhibited by some solutes in solutions.

"Almost all processes in body occur in some kind of liquid solutions."

Solutions are homogeneous mixtures of two or more substances in a single phase. Most of solutions can be considered as having a majority ingredient called a **solvent** and one or more minority ingredients called **solutes**. For the sake of simplicity in this Unit, we shall consider only binary solutions. Here each component may be in solid, liquid or in gaseous state and, therefore, several types of possible solutions are summarised in **Table 3.1**.

Table 3.1 Different Types of Solutions

Type of Solution	Common Example
Gaseous Solutions	
Gas in gas	a mixture of oxygen and nitrogen gases
Liquid in Gas	chloroform vapours mixed with nitrogen gas
Solid in Gas	camphor vapours in nitrogen gas
Liquid Solutions	
Gas in liquid	oxygen dissolved in water
Liquid in liquid	ethanol dissolved in water
Solid in liquid	sucrose dissolved in water
Solid Solutions	
Gas in solid	solution of hydrogen in palladium
Liquid in solid	amalgam of mercury with sodium
Solid in solid	copper dissolved in gold

The extent to which one component dissolves in another component differs a great deal, so much so, that the two components may be completely miscible or immiscible. During solution formation

for components having molecules of nearly equal size, the entropy factor is always favourable due to greater disorder in the solution compared to that in the pure components (Unit 4). However, to a large extent, the solubility depends upon the strength of interaction between the molecules of the pure components compared to the interaction between two different components. Thus, if $E_{A\text{-}A}$ and $E_{B\text{-}B}$ are the interaction energies between the molecules of A and molecules of B respectively and $E_{A\text{-}B}$ is the energy of interaction between molecules of A and B, then the magnitude of $2(E_{A\text{-}B}) - (E_{A\text{-}A} + E_{B\text{-}B})$ determines whether the two components are miscible, partially miscible or completely immiscible. For example, water and alcohol molecules interact very strongly with each other leading to complete miscibility while benzene and water molecules interact very weakly with the result that benzene has very low solubility in water.

In this Unit, we shall consider mostly liquid solutions and begin with various alternatives in which the concentration of a solute can be expressed in the liquid solution.

3.1 EXPRESSING CONCENTRATION OF SOLUTIONS

The composition of a solution is quantitatively specified when the amount of the solute and solvent are both known. The concentration of a solution can be expressed in a number of ways as discussed in this section.

In a solution, usually only the relative amounts of components are specified, as the properties of solutions are not governed by the absolute amounts of substances present but on their ratios. The relative amount of a solute in solution is expressed in the following ways:

Mole Fraction

Mole fraction of any component is the number of moles of that particular component divided by the sum of moles of all the components present in a solution. Mole fraction is usually denoted by the symbol x. Thus, the mole fraction, x_A of a component A in solution with another component B, is defind by :

$$x_A = \frac{n_A}{n_A + n_B}$$

Here n_A and n_B are the number of moles of components A and B, respectively, in a given quantity of the solution. For a solution obtained by mixing 46 g of ethanol and 162 g of water i.e., containing 46g/46g mol^{-1} or 1 mol of ethanol and 162g/18g mol^{-1} or 9 mol of water, the mole fraction of ethanol and water in the solution is 0.1 and 0.9, respectively.

For a solution containing i number of components, we have

$$x_1 = \frac{n_1}{n_1 + n_2 + \ldots\ldots + n_i}, \quad x_2 = \frac{n_2}{n_1 + n_2 + \ldots\ldots + n_i} \text{ etc.}$$

It can be shown that the sum of the mole fractions of all the components in a solution is unity i.e.,

$$x_1 + x_2 + \ldots\ldots + x_i = 1$$

Molality

The molality of a solution is defined as the number of moles of the solute that are present in 1 kg of the solvent.

$$\text{Molality, } m = \left[\frac{\text{Moles of solute}}{\text{Number of kilograms of solvent}}\right]$$

This unit of concentration is usually symbolized by the lower case letter m. Thus one molal aqueous solution of urea contains 60g (1 mol) of urea in 1 kg (1000 g) water. **Molality of a solution remains constant with the variation of temperature.**

Molarity

Molarity is a convenient and commonly used concentration unit about which you are already familiar (Class XI). The molarity of a solution is expressed as the number of moles of a solute present in one litre of the solution. It is designated by the symbol, M. A 0.4M aqueous solution of potassium sulphate (K_2SO_4) contains 0.4 mol of the salt in 1 litre of solution. It may be noted that the molarities of the sulphate and potassium ions in the solution are 0.4 M and 0.8 M respectively, as 1 mol potassium sulphate gives 2 mol of potassium ions and 1 mol of sulphate ions on dissociation. **Molarity of a solution changes with temperature due to accompanied change in volume of the solution.**

Example 3.1

18 g of glucose (molar mass, 180g mol^{-1}) is present in 500 cm^3 of its aqueous solution. What is the molarity of the solution? What additional data is required if the molality of the solution is also required to be calculated?

Solution

The amount of glucose present in one litre of solution $= 18g \times \frac{1000cm^3}{500cm^3} = 36g$

Number of moles of glucose present in one litre of solution $= 36g \times \frac{1\ mol}{180g} = 0.2 mol$

Thus, 0.2 mol glucose is present in one litre of solution and this by definition is the molarity of the solution.

In order to calculate the molality, we require the mass of the solvent, here the total mass for a given volume of a solution can only be determined if we know its density. The mass of the solvent is given by subtracting the mass of the solute from the mass of the solution.

Other Ways of Expressing Concentrations

The concentration of solutions is sometimes expressed in terms of percentage of one component by mass or volume present in total mass or volume of the solution. Thus, the term (w/w), usually means the mass of solute expressed in grams per 100g of solution. A 10 percent (w/w) solution of sodium chloride in water implies that 10g of sodium chloride is present in 90g of water so that the total mass of the solution is 100g. By knowing the concentration of the solution in (w/w), one can calculate the molality of a solution as well as mole fraction of each component. When a solute is present in trace quantities, it is convenient to express concentration in parts per million, abbreviated as ppm. Thus, a litre of sea water (which is 1030g) contains about 6×10^{-3} g of dissolved oxygen (O_2). Such a small concentration is also expressed as 5.8g per 10^6g (i.e., a million gram of sea water) or 5.8 ppm. The concentration of atmospheric pollutants in cities is often expressed in terms of μg/mL.

Example 3.2

An aqueous solution of sodium chloride is marked 10% (w/w) on the bottle. The density of the solution is 1.071 g mL^{-1}. What is its molality and molarity? Also, what is the mole fraction of each component in the solution?

Solution

10% (w/w) solution means that there are 10g of sodium chloride present in 90g of water. Therefore, the number of moles of NaCl in the solution is

$$= 10g \times \frac{1\ mol\ NaCl}{58.5g\ NaCl} = 0.17\ mol$$

Number of moles of water in the solution is

$$= 90g \times \frac{1\ mol\ H_2O}{18g\ H_2O} = 5.00\ mol$$

Total number of moles of both the components in the solution

$$= 5.00\ mol + 0.17\ mol$$
$$= 5.17\ mol$$

Thus, mole fraction of NaCl in the solution

$$= \frac{0.17 mol}{5.17 mol} = 0.03$$

Mole fraction of water in the solution

$$= \frac{5.00 mol}{5.17 mol} = 0.97$$

In order to calculate molality of NaCl in the solution, we have to calculate its mass in 1kg of the solvent. This mass is determined as follows:

Mass of NaCl per kilogram of the solvent (water)

$$= 10g \times \frac{1000g}{90g} = 111.11\ g$$

Number of moles of NaCl present in 1kg of water

$$= 111.11g \times \frac{1\ mol\ NaCl}{58.5g\ NaCl} = 1.90\ mol$$

Thus, *molality of the solution with respect to NaCl is 1.90 m.*

In order to calculate the molarity of the solution, we require the number of moles of NaCl present in one litre of the solution.

Mass of sodium chloride present in one litre of solution is,

$$\frac{10g}{100g} \times 1000\ mL \times 1.071\ g/mL = 107.10\ g$$

Number of moles of sodium chloride present in one litre of the solution, 107.10g/58.5 g mol^{-1} = 1.83 mol. Therefore, molarity of 10% (w/w) solution of NaCl is 1.83M.

3.2 SOLUBILITY OF GASES

We are familiar that gases are completely miscible with each other. Gases also dissolve in

liquids and solids. For example, soda-water contains carbon dioxide dissolved in water under high pressure. Oxygen is sufficiently soluble in water to allow survival of aquatic life in lakes, rivers and oceans. An example of dissolution of a gas in a solid is the solubility of hydrogen gas in palladium.

The solubility of a gas in a liquid is determined by several factors. In addition to the nature of the gas and the liquid, solubility of the gas depends on the temperature and pressure of the system. The solubility of a gas in a liquid is governed by **Henry's Law** which states that the **solubility of a gas in a liquid is directly proportional to the pressure of the gas**. Dalton, a contemporary of Henry, also concluded independently that the solubility of a gas in a liquid solution is a function of the partial pressure of the gas. If we use the mole fraction of the gas in the solution as a measure of its solubility, then:

Mole fraction of the gas in a solution is propotional to the partial pressure of the gas.
Or, partial pressure of the gas in solution
= K_H × mole fraction of the gas in solution.

Here K_H is Henry's law constant

or $p = K_H x$ (3.1)

If we draw a graph between partial pressure of the gas versus mole fraction of the gas in solution, then we should get a plot of the type as shown in Fig. 3.1.

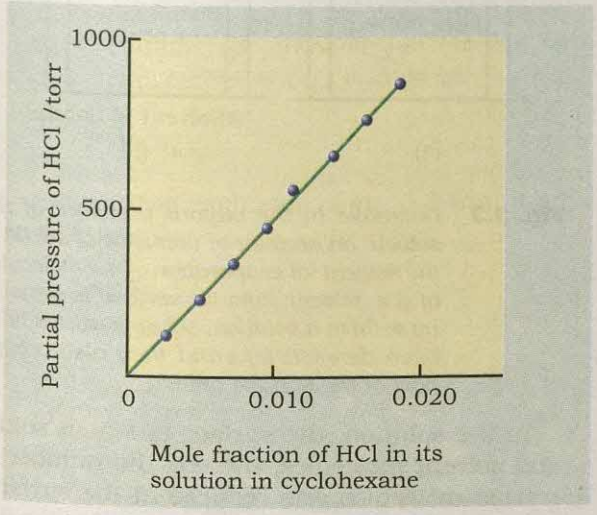


Fig. 3.1 *Experimental results for the solubility of HCl gas in cyclohexane at 293 K. The slope of the line is the Henry's Law constant, K_H.*

Different gases have different K_H values at the same temperature. This suggests that K_H is a function of the nature of the gas. Table 3.2 gives K_H values of some common gases at specified temperatures.

Table 3.2 Values of Henry's Law Constant (K_H) for some selected Gases in water

Gas	Temp/K	K_H/kbar
He	293	144.97
H_2	293	69.16
N_2	293	76.48
N_2	303	88.84
O_2	293	34.86
O_2	393	46.82

It is obvious from Eq. (3.1) that the higher the value of K_H at a given pressure, the lower is the solubiliy of the gas in the liquid. It can be seen from Table 3.2 that K_H value for both N_2 and O_2 increases with increase of temperature indicating that solubility of gases decreases with increase of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than warm waters.

Example 3.3

If N_2 gas is bubbled through water at 293K, how many millimoles of N_2 gas would dissolve in 1 litre of water. Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 kbar.

Solution

The solubility of gas is related to its mole fraction in the aqueous solution. The mole fraction of the gas in the solution is calculated by applying Henry's law. Thus,

$$x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{0.987\,\text{bar}}{76480\,\text{bar}} = 1.29\times10^{-5}$$

As 1 litre water contains 55.5 mol of it (Unit 8, Class XI), therefore, if n represents number of moles of N_2 in solution,

$$x_{N_2} = \frac{n\ \text{mol}}{n\ \text{mol} + 55.5\ \text{mol}} \approx \frac{n}{55.5} = 1.29 \times 10^{-5}$$

Thus, $n = 1.29\times10^{-5} \times 55.5\,\text{mol} = 7.16\times10^{-4}\,\text{mol}$

$$= 7.16\times10^{-4}\,\text{mol} \times \frac{1000\ m\,\text{mol}}{1\,\text{mol}}$$

$$= 0.716\ \text{m mol}$$

Henry's law finds several applications in industry and explains some biological phenomena. Notable among these are:

- To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
- To minimise the painful effects accompanying the decompression of deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.
- In lungs, where oxygen is present in air with high partial pressure, haemoglobin combines with oxygen to form oxyhaemoglobin. In tissues where partial pressure of oxygen is low, oxyhaemoglobin releases oxygen for utilization in cellular activities.

3.3 SOLID SOLUTIONS

Solid solutions are formed by mixing two solid components in the molten state in appropriate proportion and then cooling the molten mass. Solid solutions are of two types: substitutional solid solutions and interstitial solid solutions. In a substitutional solid solution, atoms, molecules or ions of one substance take the place of similar species of other substance in its crystal lattice as shown in [Fig. 3.2(a)]. Brass, bronze, monel metal and steel are familiar examples of this type of solid solution.

Interstitial solid solutions constitute the other type and are formed by placing atoms of one kind into voids or interstices, that exist between atoms in the host lattice. This is illustrated in [Fig. 3.2(b)].

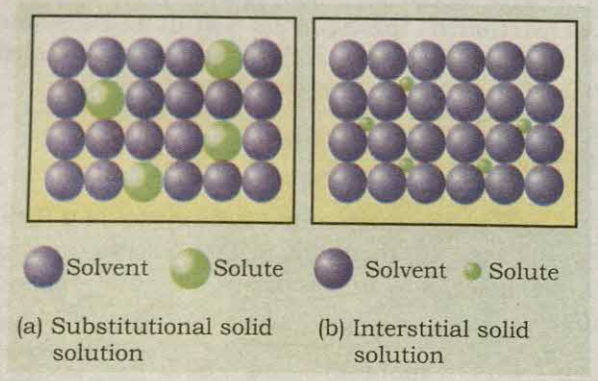


Fig. 3.2 *Two types of solutions (a) substitution solid solution in which particles of the solute replace particles in the host lattice (the solvent) (b) an interstitial solid, solution in which the solute particles fit in spaces between particles of the host lattice (the solvent).*

Tungsten carbide, WC, an extremely hard substance, is an example of interstitial solid solution. Here tungsten atoms are arranged in a face-centred cubic pattern with carbon atoms in the octahedral holes where these are surrounded by six tungsten atoms placed at the vertices of the octahedron. Tungsten carbide has many industrial uses in making of cutting and grinding tools.

3.4 SOLUTIONS OF SOLIDS IN LIQUIDS AND THEIR VAPOUR PRESSURE

This is the most common class of solutions formed by the dissolution of solid in liquids such as sodium chloride, glucose, urea and cane sugar in water, and iodine and sulphur in carbon disulphide. It is well known that the pressure exerted by a liquid at a given temperature is called its **vapour pressure** [Fig. 3.3(a)]. If a non-volatile solute is added to a solvent to give a solution [Fig. 3.3(b)], the vapour pressure of the solution is solely from the solvent alone. This vapour pressure of the solution is found to be lower than the vapour pressure of the pure solvent.

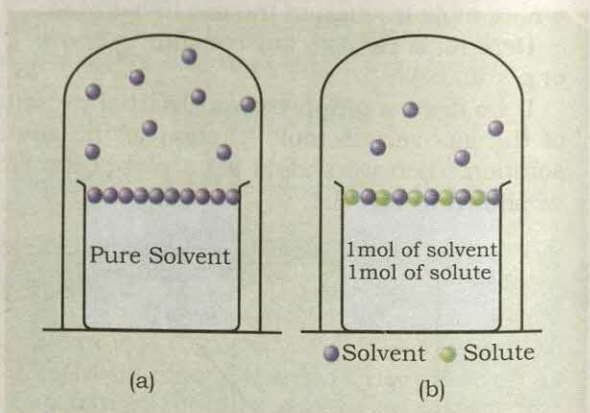


Fig. 3.3 *Decrease in the vapour pressure of the solvent on account of presence of solute in the solvent (a) evaporation of the molecules of the solvent from its surface is denoted by ●, (b) in a solution, solute particles have been denoted by ● and they also occupy part of the surface area.*

In the solution, the surface has both solute and solvent molecules, thereby the number of solvent molecules gets reduced at the surface. Consequently, the number of solvent molecules escaping from the surface is correspondingly reduced and this results in the decrease of vapour pressure of the solvent.

3.4.1 Vapour Pressure of Solution and Raoult's Law

The French Chemist Francois Marie Raoult in (1886) observed that partial vapour pressure of a solvent over a solution of a nonvolatile solute, $p_{solution}$ is directly proportional to the mole fraction of the solvent in the solution (Fig. 3.4).

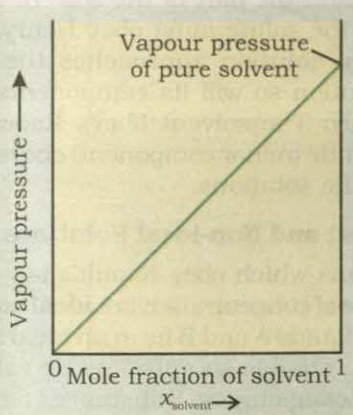


Fig. 3.4 *If a solution obeys Raoult's law for all concentrations, its vapour pressure would vary linearly from zero to the vapour pressure of the pure solvent.*

Mathematically such a relationship is described as

$$p_{solution} = x_{solvent}\, p^{\circ}_{solvent} \qquad (3.2)$$

Where $p^{\circ}_{solvent}$ is the vapour pressure of the pure solvent at the given temperature.

This relationship is known as Raoult's Law and rearrangement of Eq. (3.2) gives

$$\frac{p_{solution}}{p^{\circ}_{solvent}} = x_{solvent} \qquad (3.3)$$

Subtracting each side of eq. 3.3 from unity, results into

$$1 - \frac{p_{solution}}{p^{\circ}_{solvent}} = 1 - x_{solvent} = x_{solute} \qquad (3.4)$$

$$\text{or} \quad \frac{(p^{\circ}_{solvent} - p_{solution})}{p^{\circ}_{solvent}} = x_{solute} \qquad (3.5)$$

In eq. 3.5 $p^{\circ}_{solvent} - p_{solution}$ represents the lowering of vapour pressure on the formation of the solution and the term $(p^{\circ}_{solvent} - p_{solution})/p^{\circ}_{solvent}$ is called **the relative lowering of vapour pressure** of the solution. Thus the statement of Raoult's law for solutions of nonvolatile solutes is: **The relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute which is a non-volatile nonelectrolyte.** This relative lowering of vapour pressure is a colligative property which depends on mole fraction of the solute.

3.4.2 Raoult's Law for a Solution containing Volatile Components

What happens when the solute and solvent both are volatile? Here, the vapour phase consists of the vapours of both the components present in the solution. We should then expect the partial vapour pressure of each component of the solution to depend on the mole fraction of the corresponding component. Let us consider a solution in which both the components obey Raoult's law marked as A and B with their mole fraction x_A and x_B, respectively. Their partial vapour pressures p_A and p_B are proportional to the respective mole fractions in the solution. Thus,

$$p_A \propto x_A$$

Similarly, $$p_B \propto x_B$$

Based on experimental findings, Raoult proposed that in case of mixture of two miscible liquids, the above relation written as follows holds good.

$$p_A = p^{\circ}_A x_A$$

$$p_B = p^{\circ}_B x_B$$

Where p°_A and p°_B represent the vapour pressures of pure components A and B respectively. The relationship between vapour pressure of a component and its mole fraction is another form of Raoult's Law. This can be stated as: **for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.** The law is applicable only when the two volatile liquids form a homogeneous solution.

A plot of p_A or p_B against x_A or x_B for a solution should give a straight line (Fig. 3.5).

These lines pass through the points p^0_A or p^0_B when x_A and x_B equals unity. According to Dalton's law of partial pressure, the total

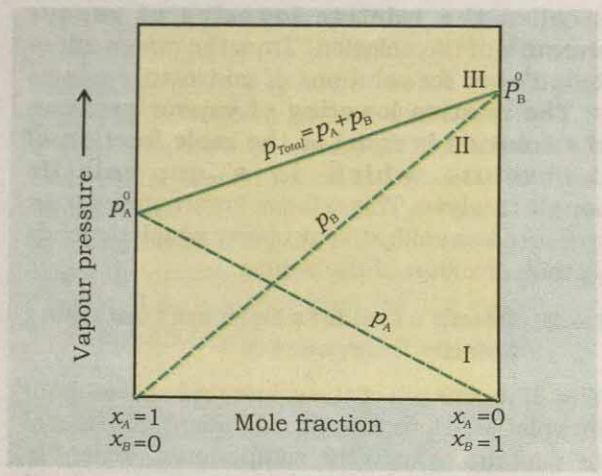


Fig. 3.5 *The relationship between vapour pressure and mole fraction of an ideal solution at constant temperature. The dashed lines I and II represent the partial pressure of the components. (It can be seen from the plot that p_A and p_B are directly proportional to x_A and x_B, respectively). The total vapour pressure is given by line marked III in the figure.*

pressure of the solution for any composition is given as

$$p_{Total} = p_A + p_B \qquad (3.6)$$

Here, p_{Total} is indicated in Fig. 3.5 by line III, obtained by joining the points p_A^0 and p_B^0.

Solutions obeying Raoult's Law are called **ideal liquid solutions**. Evidently for such solutions, the vapour pressure are intermediate between the values, p_A and p_B and they all lie on the straight line joining p_A^0 and p_B^0 (Fig. 3.5).

Raoult's Law as a Special Case of Henry's Law:

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by $p_A = p_A^0 x_A$. In the solution of a gas in a liquid, the gaseous component is so volatile that it exists as a gas and we have already seen that its solubility is governed by Henry's law that states that $p = K_H x$.

If we compare the equations for Raoult's law and Henry's law, it can be seen that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution. Only the proportionality constant K_H differs from p_A^0. Thus, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_A^0. Even in liquid solutions, sometimes, one of the components may obey Henry's law over a range of mole fraction. In practice, in the solution in which the solute behaves ideally according to Henry's law, the solvent also behaves ideally according to Raoult's law (though the reverse is not necessarily true and Raoult's law ideality on the part of the solvent does not mean that the solute must obey Henry's law).

As a real solution approaches the limit of infinite dilution so will its components behave more ideally. The solvent obeys Raoult's Law whereas solute (minor component) obeys Henry's law for dilute solutions.

3.4.3 Ideal and Non-ideal Solutions

The solutions which obey Raoult's law over the entire range of concentration are **ideal solutions**. When two liquids A and B form an ideal solution, there is no change in enthalpy or volume on mixing the components. Substances forming an ideal solution have similar structures. A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. Examples of ideal solutions are: mixture of hexane and heptane; ethyl bromide and ethyl chloride; benzene and toluene; and chlorobenzene and bromobenzene.

When a solution does not obey Raoult's law then it is called a **non-ideal solution**. We will now discuss more about nonideal solutions.

Non-ideal Solutions

Actually very few solutions obey Raoult's law. Usually the measured vapour pressure of the solution is either higher or lower than that predicted by Raoult's law. If this vapour pressure is higher, the solution is considered to show **positive deviation** from Raoult's law. On the other hand if the vapour pressure is lower than predicted by Raoult's law, the solution exhibits **negative deviation**. The examples of solutions showing positive and negative deviations from Raoult's law are shown in Fig. 3.6(a) and 3.6(b).

The cause for these deviations lies in the nature of interactions at the molecular level. On mixing two dissimilar substances, their molecular environment will change. Suppose the two components that are mixed to form a nonideal solution are A and B. A positive deviation is exhibited when interaction between A– B is weaker than that betwen A–A and B–B. This means that on mixing, molecules of A (or of

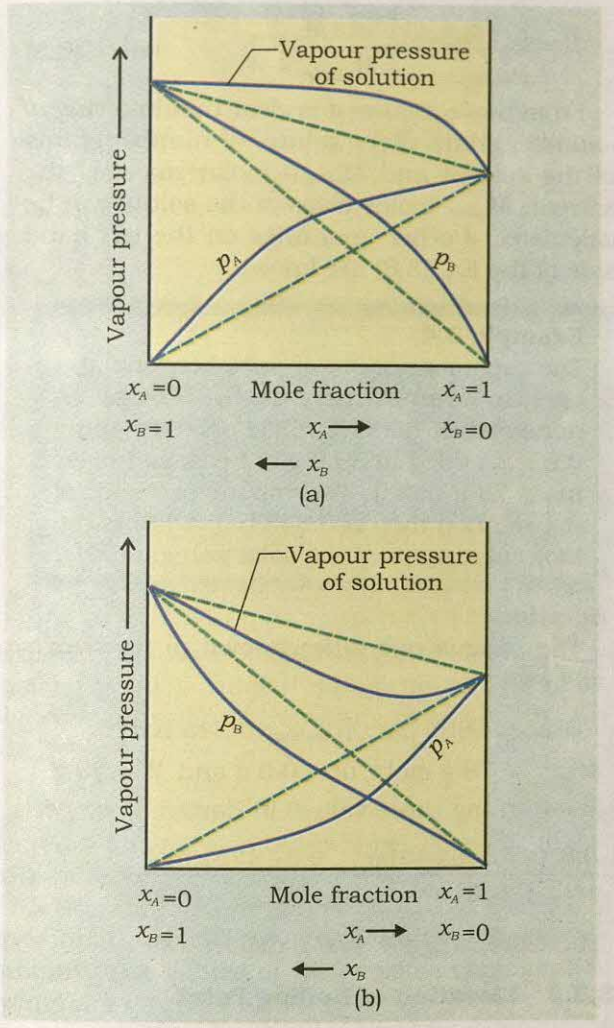
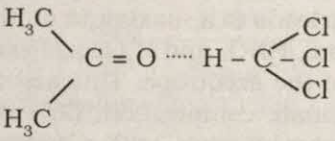


Fig. 3.6 *The vapour pressures of two components system as a function of composition (a) A solution that shows positive deviation from Raoult's law (b) A solution that shows negative deviation from Raoult's law.*

B) will find it easier to escape than if these were as pure components. This will cause increase in the vapour pressure resulting in a positive deviation. Mixtures of ethanol and acetone behave in this way. In pure ethanol, molecules are hydrogen bonded. On adding acetone, these molecules get in between the host molecules breaking the hydrogen bonds of host molecules. This changes the intermolecular interaction pattern and becomes the cause for ethanol and acetone solution to behave nonideally and show a positive deviation from Raoult's law.

A mixture of chloroform and acetone forms a solution with negative deviation from Raoult's law. This is because chloroform molecule is able to form hydrogen bond with acetone molecule as shown in the following manner.



This decreases the escaping tendency of molecules for each component and consequently, the vapour pressure decreases resulting in negative deviation from Raoult's law.

Some liquids on mixing form azeotropes which are binary mixtures having same composition in liquid and vapour phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called as **minimum boiling azeotrope** and **maximum boiling azeotrope**, respectively. Solutions of ethanol and water show such a large deviation from Raoult's law that there is a maximum in the vapour pressure curve and hence a minimum in the boiling point diagram as shown in Fig. 3.7.

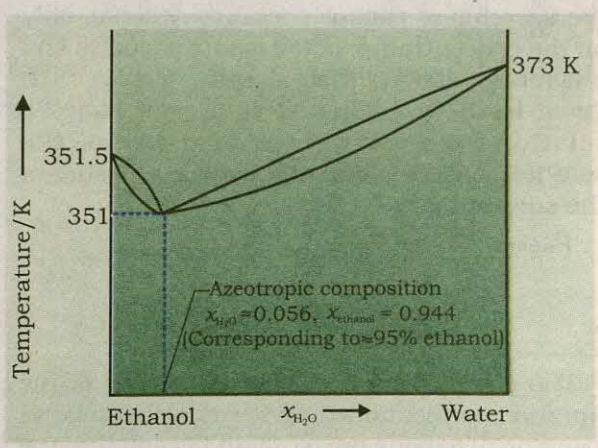


Fig. 3.7 *The boiling point diagram for ethanol-water mixtures (not drawn to scale).*

Ethanol-water mixtures (obtained by fermentation of sugars) are rich in water. Fractional distillation is able to concentrate the alcohol to at best, the azeotropic composition of approximately 95% by volume of ethanol. Once this composition has been achieved, the liquid and vapour have the same composition, and no additional fractionation occurs. Other methods of separation have to be used for preparing 100% C_2H_5OH.

There are also solutions that show large negative deviation from ideality and, therefore, have a minimum in their vapour pressure curves. This leads to a maximum on the boiling point diagram. HNO_3 and H_2O form examples of this class of the azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393 K.

3.5 COLLIGATIVE PROPERTIES AND DETERMINATION OF MOLECULAR MASS

A Colligative property of a solution is one that depends on the number of particles dissolved in it, rather than on the chemical identity of particles. Examples of such properties are (i) the relative lowering of vapour pressure of the solvent (ii) the elevation of boiling point of the solvent (iii) the depression of freezing point of the solvent and (iv) the osmotic pressure of the solution.

3.5.1 Relative Lowering of Vapour Pressure

We have seen in Section 3.4 that the vapour pressure of a solvent in a solution is less than that of the pure solvent. Raoult established that the lowering of vapour pressure depends only on the concentration of the solute particles and it is independent of their identity. The Eq. (3.2) given in the previous section establishes a relation between vapour pressure of the solution, mole fraction and vapour pressure of the solvent i.e.,

$$p_{solution} = x_{solvent}\, p^{\circ}_{solvent}$$

or

$$\frac{(p^{0}_{solvent} - p_{solution})}{p^{0}_{solvent}} = x_{solute}$$

The expression on the left hand side of the equation as mentioned earlier is called relative lowering of vapour pressure and is equal to the mole fraction of the solute.

The above equation may be rewritten as:

$$\frac{p^{0}_{solvent} - p_{solution}}{p^{0}_{solvent}} = n/(n+N)$$

Here n and N are the number of moles of solute and solvent, respectively.

or

$$\frac{p^{0}_{solvent} - p_{solution}}{p^{0}_{solvent}} = \frac{w}{M_{solute}} \Big/ \left(\frac{w}{M_{solute}} + \frac{W}{M_{solvent}}\right) \quad (3.7)$$

For dilute solutions $n << N$, and neglecting n in denominator we have

$$\frac{p^{0}_{solvent} - p_{solution}}{p^{0}_{solvent}} = \frac{w \times M_{solvent}}{M_{solute} \times W} \quad (3.8)$$

From this equation it is clear that knowing w –number grams of the solute, W–number grams of the solvent and $M_{solvent}$– molar mass of the solvent; M_{solute}–molar mass of the solute can be calculated if other quantities on the left hand side of the Eq. (3.8) are known.

Example 3.4

The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, nonelectrolyte solid weighing 0.5 g is added to 39.0 g of benzene (molar mass 78 g mol^{-1}). The vapour pressure of the solution then is 0.845 bar. What is the molecular mass of the solid substance?

Solution

The various quantities known to us are as follows:

$p^{0}_{solvent}$ = 0.850 bar; $p_{solution}$ =0.845 bar;

$M_{solvent}$ = 78 g mol^{-1}; w = 0.5 g and W = 39 g

Substituting these values in Eqn. 3.8, we get

$$\frac{0.850\,\text{bar} - 0.845\,\text{bar}}{0.850\,\text{bar}} = \frac{0.5\,\text{g} \times 78\,\text{g mol}^{-1}}{M_{solute} \times 39\,\text{g}}$$

Therefore, M_{solute} = 170 g mol^{-1}.

3.5.2 Elevation of Boiling Point

We have noted above that the presence of a solute lowers the vapour pressure of a solvent. Vapour pressure of water is 1.013 bar at 373.15K (100°C). Water, therefore, boils at 373.15K as its vapour pressure at this temperature becomes equal to one atmospheric pressure which is 1.013 bar. The vapour pressure of an aqueous solution of sucrose is less than 1.013 bar at 373.15K and consequently the solution will not boil at 373.15K. In order to make the solution boil, its vapour pressure must be increased to 1.013 bar by further raising the temperature above the boiling point of the pure solvent (water). Thus, boiling point of a solution is always higher than the boiling point of the pure solvent in which solution is prepared (Fig. 3.8). Like the lowering of vapour pressure, the boiling point elevation depends on the nature of the solvent. A solution of 1 mol of sucrose in 1000g of water boils at 373.52K at 1 atmospheric pressure.

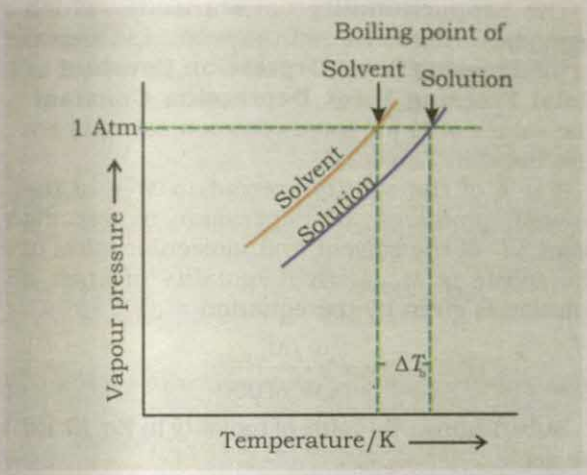


Fig. 3.8 *The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.*

Experiments have shown that the elevation of boiling point is directly proportional to the molal concentration of the solute in a solution. Thus,

$$\Delta T_b \propto m$$

or, $$\Delta T_b = K_b\, m \qquad (3.9)$$

Here, m (molality) is the number of moles of solute in 1 kg of solvent and the constant of proportionality, K_b is called **Boiling Point Elevation Constant or Molal Boiling Point Constant.** The values of K_b for some common solvents are given in Table 3.3.

Table 3.3 Molal Boiling Point Elevation and Freezing Point Depression constants for some solvents.

Solvent	b.p./K	K_b/ (K kg mol^{-1})	f.p./K	K_f/ (K kgmol^{-1})
Water	373.15	0.52	273.0	1.86
Ethanol	351.5	1.20	155.7	1.99
Cyclohexane	353.74	2.79	279.55	20.00
Benzene	353.3	2.53	278.6	5.12
Chloroform	334.4	3.63	209.6	4.70
Carbon-tetrachloaride	350.0	5.03	250.5	31.8
Carbon-disulphide	319.4	2.34	164.2	3.83
Diethyl ether	307.8	2.02	156.9	1.79
Acetic acid	391.1	2.93	290.0	3.90

If w gram of solute of molar mass, M_{solute} is present in W gram of solvent, then molality, m of solution is given by the expression:

$$m = \frac{w / M_{solute}}{W / 1000} = \frac{1000 \times w}{M_{solute} \times W}$$

Substituting the value of molality in Eq. (3.9), we get

$$\Delta T_b = \frac{K_b \times 1000 \times w}{M_{solute} \times W} \qquad (3.10)$$

$$M_{solute} = \frac{K_b \times 1000 \times w}{\Delta T_b \times W} \qquad (3.11)$$

Thus, in order to determine M_{solute}, molecular mass of the solute, a known mass of the solute in a known mass of the solvent is taken and ΔT_b is determined experimentally for a known solvent (solvent whose K_b value is known).

Example 3.5

18g of glucose, $C_6H_{12}O_6$, is dissolved in 1 kg of water in a saucepan. At what temperature will the water boil (1.013 bar pressure). K_b for water is 0.52 K kg mol^{-1}.

Solution

Number of moles of glucose

$$= \frac{18\text{g}}{180\text{g mol}^{-1}} = 0.1\text{mol}$$

Number of kilograms of solvent = 1 kg

Thus, the molality of glucose solution

$$= \frac{0.1\text{mol}}{1\text{kg water}} = 0.1\,\text{mol kg}^{-1} = 0.1\,\text{m}$$

For water, change in boiling point

$$\Delta T_b = K_b \times m = 0.52\text{K kg mol}^{-1} \times 0.1\,\text{mol kg}^{-1}$$

$$= 0.052\ \text{K}$$

Since water boils at 373.15 K at 1.013 bar pressure, therefore, the boiling point of solution will be 373.15 + 0.052 = 373.202 K.

Example 3.6

The boiling point of benzene is 353.23K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute. K_b for benzene is 2.53 K kg mol^{-1}.

Solution

The elevation (ΔT_b) in the boiling point = 354.11K – 353.23K = 0.88K

Substituting these values in expression. (3.11), we get

$$M_{solute} = \frac{2.53\,K\,kg\,mol^{-1} \times 1.8g}{0.88K \times (90/1000)\,kg} = 58g\,mol^{-1}$$

Therefore, molar mass of the solute, M_{solute} = 58 g mol^{-1}.

3.5.3 Depression of Freezing Point

The lower vapour pressure of a solution causes a lowering of the freezing point compared to that of the pure solvent (Fig. 3.9).

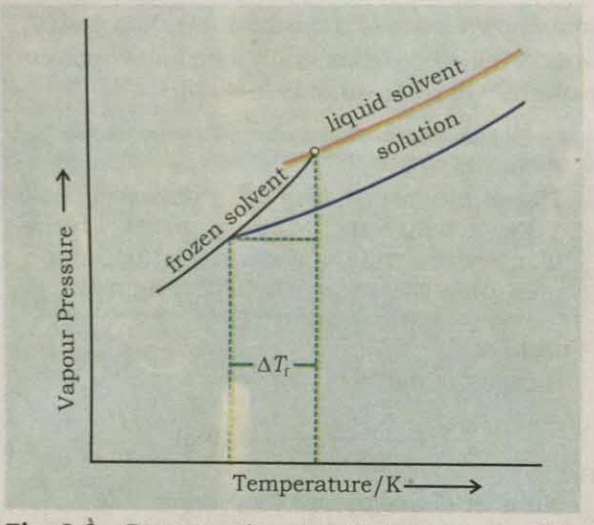


Fig. 3.9 *Diagram showing ΔT_f depression of the freezing point of a solvent in a solution.*

We know that at the freezing point of a solvent, the solid and the liquid are in equilibrium. This is possible only if they have the same vapour pressure. A solution will freeze when its vapour pressure equals the vapour pressure of pure solid solvent. For this it is necessary to lower the temperature of the solution. This is possible when the solution freezes at a lower temperature when the vapour pressure of the pure solid is equal to the vapour pressure of the solvent over the solution. This leads to lowering of freezing point.

Similar to elevation of boiling point, depression of freezing point, ΔT_f, is directly proportional to molality, m of the solution. Thus,

$\Delta T_f \propto m$, or

$$\Delta T_f = K_f m \qquad (3.12)$$

The proportionality constant, K_f, which depends on the nature of the solvent is known as the **Freezing Point Depression Constant or Molal Freezing Point Depression Constant**. The values of K_f for some common solvents are also listed in Table 3.3.

If w g of the solute, present in W g of the solvent, produces the depression in freezing point ΔT_f of the solvent and molecular mass of the solute is M_{solute}, then molality of such a solution is given by the equation

$$m = \frac{w/M_{solute}}{W/1000}$$

Substituting this value of molality in Eq. (3.12) we get

$$\Delta T_f = \frac{K_f \times w/M_{solute}}{W/1000} \qquad (3.13)$$

$$\text{or } \Delta T_f = \frac{K_f \times 1000 \times w}{M_{solute} \times W}$$

$$M_{solute} = \frac{K_f \times 1000 \times w}{\Delta T_f \times W} \qquad (3.14)$$

Thus far determining the molecular mass (or molar mass) of the solute we should know the quantities w, W, ΔT_f alongwith the molal freezing point depression constant.

The values of K_b and K_f which are functions of the nature of the solvent can be ascertained from the following relations.

$$K_b = \frac{RT_b^2}{1000\Delta_{vap}H/M_{solvent}} \qquad (3.15)$$

$$K_f = \frac{RT_f^2}{1000\Delta_{fus}H/M_{solvent}} \qquad (3.16)$$

Here the symbols R and $M_{solvent}$ stand for gas constant and molar mass of the solvent, respectively and T_b and T_f denote the boiling point and freezing point of the solvent, respectively in kelvin. Further, $\Delta_{vap}H$ and $\Delta_{fus}H$ represent change in enthalpies for the vaporisation of the solvent and fusion of the pure solid solvent, respectively.

Example 3.7

45g of ethylene glycol $C_2H_6O_2$ is mixed with 600 g of water. Calculate (a) the freezing point depression and (b) the freezing point of the solution.

Solution

Depression in freezing point is related to the molality, therefore, the molality of the solution with respect to ethylene glycol

$$= \frac{\text{moles of ethylene glycol}}{\text{kg of water}}$$

Moles of ethylene glycol

$$= 45\text{g} \times \frac{1\text{mol}}{62\text{g}} = 0.73\text{mol}$$

$$\text{Mass of water in kg} = 600\text{g} \times \frac{1\text{kg}}{1000\text{g}} = 0.60\text{kg}.$$

Hence, molality of ethylene glycol

$$= \frac{0.73\text{mol}}{0.60\text{kg}} = 1.20\text{mol kg}^{-1}$$

Therefore freezing point depression,

$\Delta T_f = 1.86\text{K kg mol}^{-1} \times 1.2 \text{ mol kg}^{-1} = 2.2 \text{ K}$

Freezing point of the aqueous solution

$= 273.15 \text{ K} - 2.2\text{K}$

$= 270.95 \text{ K}.$

Example 3.8

1.00 g of a nonelectrolyte solute dissolved in 50.0 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is 5.12 K kg mol^{-1}. Find the molecular mass of the solute.

Solution

Substituting the value of the various terms involved in eq. 3.13, we get

$$M_{solute} = \frac{5.12\text{K kg mol}^{-1} \times 1.00\text{g}}{0.40\text{K} \times 50\text{g}/1000\text{g kg}^{-1}} = 256\text{g mol}^{-1}$$

Thus, molecular mass of the solute = 256 g mol^{-1}.

3.5.4 Osmosis and Osmotic Pressure

Osmosis is the phenomenon in which a solution separated from the solvent by a semipermeable membrane (permeable only to solvent molecules) allows the flow of the solvent into the solution. This also happens when two solutions of different concentrations in the same solvent are separated by the membrane. In this case, the solvent flows from a solution of lower concentration to the solution of higher concentration. This process continues till the concentration on both sides of the membrane becomes equal. The flow of the solvent from its side to solution side separated by semipermeable membrane can be stopped if some definite extra pressure is applied on the solution. This pressure that just stops the flow of solvent is called *osmotic pressure* of the solution and the process of flow of solvent is called *osmosis*. This pressure has been found to depend on the concentration of the solution. Osmosis is a process of prime importance in living organisms. The salt concentration in blood plasma due to different species is equivalent to 0.9% of aqueous sodium chloride has by mass. If blood cells are placed in pure water, water molecules rapidly move into the cell. The movement of water molecules into the cell dilutes the salt content. The blood cells as a result of this transfer of water molecules, swell and burst. Hence care is always taken to ensure that solutions that flow into the blood stream are of the same osmotic pressure as that of the blood. Sodium ion, Na^+ and potassium, K^+ ions, are responsible for maintaining proper osmotic pressure balance inside and outside of the cells of organism. Osmosis is also critically involved in the functioning of kidneys.

The osmotic pressure of a solution is the excess pressure that must be applied to the solution to prevent osmosis i.e., to stop the passage of solvent molecules through a semipermeable membrane into the solution. This is illustrated in Fig. 3.10.

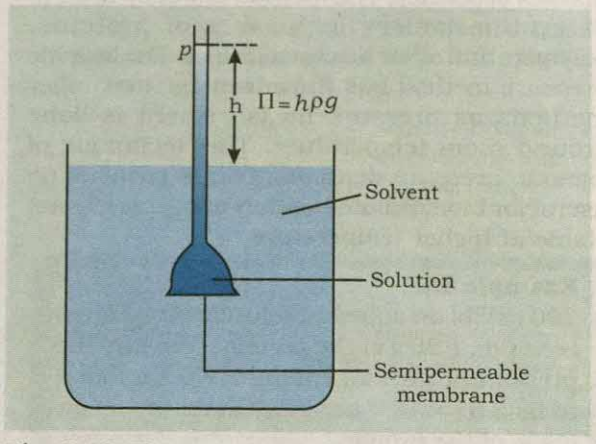


Fig. 3.10 *The principle of measuring osmotic pressure. The pressure in excess of atmospheric pressure that must be applied to the solution to prevent it from rising in the tube is the osmotic pressure. This will also be equal to hydrostatic pressure of the liquid column of height, h.*

The solutions having the same osmotic pressure are called **isotonic solutions**. *The osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity.* For dilute solutions, it has been found experimentally that the **osmotic pressure is proportional to the molarity, *M* of the solution at a given temperature *T***. Thus,

$$\Pi = MRT \qquad (3.17)$$

Here Π is the osmotic pressure and R is the gas constant.

$$\text{Or } \Pi = \frac{n}{V}RT \qquad (3.18)$$

Where V is the volume of a solution in litres containing n moles of the solute.

If w g of the solute whose molecular mass is M_{solute} be present in the solution then $n = w/M_{solute}$ and we can write,

$$\Pi V = \frac{w}{M_{solute}}.RT \qquad (3.19)$$

Equation 3.19 on rearrangement gives:

$$M_{solute} = \frac{wRT}{\Pi V} \qquad (3.20)$$

Thus, knowing quantities w, T, Π and V, molecular mass of the solute, M_{solute} can be calculated.

Measurement of osmotic pressure provides another method of determining molecular masses of solutes. The method is widely used to determine molecular masses of proteins, polymers and other macromolecules. The osmotic pressure method has the advantage over other methods as pressure measurement is done around room temperature. This technique of osmotic pressure determination is particularly useful for biomolecules as they are generally not stable at higher temperature.

Example 3.9

200 cm^3 of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molar mass of the protein.

Solution

The various quantities known to us are as follows:

$\Pi = 2.57 \times 10^{-3}$ bar, $V = 200$ cm^3
$= 0.200$ litre

$T = 300$ K, $R = 0.083$ L bar mol^{-1} K^{-1}

Substituting these quantities in equation 3.20, we get

$$M_{solute} = \frac{1.26\,g \times 0.083\,L\,bar\,mol^{-1}\,K^{-1} \times 300K}{2.57 \times 10^{-3}\,bar \times 0.200L}$$

$$= 61022\ g\ mol^{-1}$$

Thus, molar mass of the protein is 61022 g mol^{-1}.

Reverse Osmosis and Water Purification

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semipermeable membrane (SPM). This phenomenon is called reverse osmosis and is of great practical utility. Reverse osmosis is used in the **desalination** of sea water. A schematic set up for the process is shown in (Fig. 3.11). When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane. A variety of polymer membranes are available for this purpose.

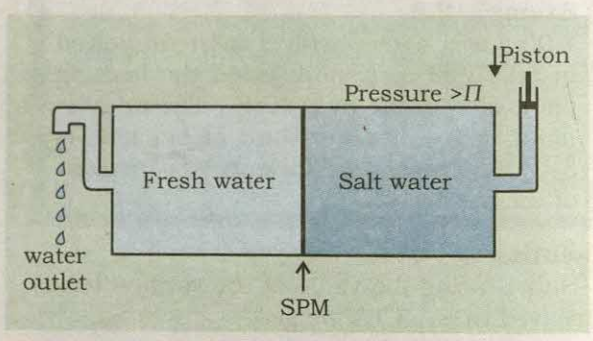


Fig. 3.11 *Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.*

The pressures required for reverse osmosis are quite high and a workable porous membrane is a film of cellulose acetate placed over a suitable support. Cellulose acetate is permeable to water but impermeable to impurities and ions present in sea water. These days many countries use desalination plants to meet their water requirement.

3.6 ABNORMAL MOLECULAR MASS

Experiments on colligative properties of solutions reveal trustworthy results only if the following two conditions are met.

(i) The Solution used must not be too Concentrated

If solution is concentrated, particles begin to interact with each other as much as with the solvent. This obviously means that the vapour pressure starts to depend on the nature of the solute, and not just on the number of solute particles. Equations derived for molecular mass determination are based on the assumption that solution is ideal.

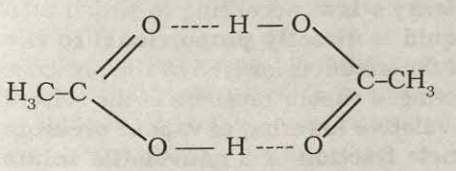
(ii) The Solute must not Dissociate or Associate

Discrepancies in determination of molecular mass arise when molecules of solute dissociate or associate on dissolving in a solvent.

We know that ionic compounds when dissolved in water dissociate (Unit 8, Class XI) into cations and anions. For example if we dissolve 1 mol of KCl (74.5 g), in water, we expect 1 mol of K^+ and 1 mol Cl^- to be released in the solution. If this happens, there would be 2 mol of particles in the solution. If we ignore interionic attraction, 1 mol KCl in one kg of water would be expected to increase the boiling point by 2 × 0.52 K = 1.04K. Now if we did not know about the dissociations into ions, we could be led to conclude that the mass of 2 mol particles is 74.5 and the mass of 1 mol of KCl is 37.25. This brings into light the rule that, when there is dissociation into ions, the experimentally determined mass is always lower than the true value. This discrepancy in the molecular mass is called as *abnormal molecular mass*.

Molecules of ethanoic acid (acetic acid) dimerise in bezene due to hydrogen bonding. This normally happens in solvents of low dielectric constant. In this case the number of particles is reduced due to dimerisation. Here the mass is more than the actual value of the solute. Association of molecules is depicted as follows:

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$



It can be undoubtedly stated here that if all the molecules of ethanoic acid associate in benzene, then ΔT value for ethanoic acid will be half of the normal value. The molar mass calculated on the basis of this ΔT will, therefore, be twice the expected value.

In 1886 Van't Hoff introduced a factor i, known as the Van't Hoff factor, to account for the extent of dissociation or association. This factor i is defined as:

$$i = \frac{\text{Normal molecular mass}}{\text{Abnormal molecular mass}} \qquad (3.21)$$

Here abnormal molecular mass is the experimentally determined molecular mass. In case of association, values of i are less than unity while for dissociation its values are greater than unity. For example, the value of i for aqueous KCl solution is close to 2 while the value for ethanoic acid in benzene is nearly 0.5.

Inclusion of the Van't Hoff factor modifies the equations for the colligative properties as follows:

Relative lowering of vapour pressure of the solvent,

$$\frac{p^0_{\text{solvent}} - p_{\text{Solution}}}{p^0_{\text{solvent}}} = i\left(\frac{n}{N+n}\right)$$

Elevation of Boiling point, $\Delta T_b = iK_b m$

Depression of Freezing point, $\Delta T_f = i\,K_f m$

Osmotic pressure of solution $\Pi = i\,nRT/V$

Table 3.4 depicts values of the factor, i for several strong electrolytes. For NaCl, KCl and $MgSO_4$, i approaches 2 as the solution becomes very dilute. As expected, the value of i gets close to 3 for K_2SO_4.

Table 3.4 Values of Van't Hoff Factor, i, at various concentrations for NaCl, KCl, $MgSO_4$ and K_2SO_4

	* Values of i			Van't Hoff Factor i for complete dissociation
Salt	0.1*m*	0.01*m*	0.001*m*	of solute
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
$MgSO_4$	1.21	1.53	1.82	2.00
K_2SO_4	2.32	2.70	2.84	3.00

* represent i values for incomplete dissociation.

Example 3.10

2 g of C_6H_5COOH dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molar depression constant for benzene is 4.9 K kg mol^{-1}. What is the percentage association of acid if it forms double molecules (dimer) in solution?

Solution

The given quantities are:

$w = 2g$; $K_f = 4.9K\ kg\ mol^{-1}$

$W = 25g$; $\Delta T_f = 1.62\ K$

Substituting these values in equation 3.13,

we get, $$M_{solute} = \frac{4.9K\ kg\ mol^{-1} \times 2g}{25/1000\ kg \times 1.62K}$$

$$= 241.98g\ mol^{-1}$$

Thus, experimental molar mass of benzoic acid in benzene = 241.98g

Now consider the following equilibrium for the acid:

$$2\ C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$

If x represents the degree of association of the solute then we would have $(1-x)$ mol of benzoic acid left unassociated and correspondingly $x/2$ as associated moles of benzoic acid at equilibrium. Therefore, total number of moles of particles at equilibrium is:

$$1 - x + \frac{x}{2} = 1 - \frac{x}{2}$$

This total number of moles of particles at equilibrium equals Van't Hoff factor i.

$$\text{But, } i = \frac{\text{Normal molecular mass}}{\text{Abnormal molecular mass}} = \frac{122}{241.98}$$

Thus

$$\frac{122}{241.98} = 1 - \frac{x}{2}$$

$$\text{or } \frac{x}{2} = 1 - \frac{122}{241.98} = \frac{241.98 - 122}{241.98}$$

$$\text{or } x = \frac{239.96}{241.98} = 0.992 = 99.2\%$$

Therefore, degree of association of benzoic acid in benzene is 99.2 percent.

Three Landmark Discoveries on the Behaviour of Solutions

Francois Marie Raoult gave a relationship between the formula mass of a dissolved substance and its vapour pressure in a dilute solution. Raoult emphasised that certain characteristic physical properties of solutions depend on the choice of the solvent rather than on the choice of the solute. He was professor at the French university of Grenoble, and although a number of scientists of the day had extensively worked on the effects of solutes on solutions, his was the definitive work.

J.H. Van't Hoff

Jacobus Henricus Van't Hoff, a Dutch physical chemist, observed that electrolytes solutions consistently deviate from the behaviour predicted by Raoult. Sodium chloride solution, for example, produced nearly twice as large a colligative effect as sugar solutions, behaving as though there were twice as many moles of particles present in solution. Van't Hoff is the first Noble laureate in chemistry for the discovery of the laws of chemical dynamics and of osmotic pressure in 1901.

Svante Arrhenius explained the observations made by Van't Hoff regarding colligative properties on the basis of dissociation of electrolytes into oppositely charged ions. For this contribution he was awarded the Nobel Prize for Chemistry in 1903.

SUMMARY

A solution is a homogeneous mixture of two or more substances. Solutions are classified into solid, liquid and gaseous solutions. The concentration of a solution is expressed in terms of mole fraction, molality, molarity and in percentages. The dissolution of a gas in a liquid is governed by **Henry's law**, according to which at a given temperature the **solubility of a gas in a liquid is directly proportional to the partial pressure of the gas**. The vapour pressure of the solvent is lowered by the presence of a nonvolatile solute in the solution and this lowering of vapour pressure of the solvent is governed by Raoult's law, according to which the **relative lowering of vapour pressure of the solvent over a solution is equal to the mole fraction of a nonvolatile solute present in a solution**. However, in a binary liquid solution, if both the components of the solution are volatile then another form of Raoult's law is used. Mathematically, this form of the Raoult's law is stated as : $p_{Total} = p_A^0\ x_A + p_B^0\ x_B$. **Solutions which obey Raoult's law over the entire range of concentration are called ideal**

solutions. Two types of deviations from Raoult's law called as positive and negative deviations are observed. Azeotropes arise due to very large deviations from Raoult's law.

Properties of solutions that depend only on the number of solute particles and are independent of the chemical identity of the solute, such as the relative lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure are known as colligative properties. The osmosis process can actually be reversed if a pressure higher than the osmotic pressure is applied to the solution . Colligative properties have been used to determine the molecular masses of solutes of various kinds. Solutes which dissociate in the solution, exhibit molecular mass less than the actual molecular mass and those which associate show more molecular mass than their actual values.

Quantitatively, the degree to which a solute behaves as though it were dissociated or associated can be expressed by the Van't Hoff factor i. This factor has been defined as ratio of normal molecular mass to experimentally determined molecular mass.

EXERCISES

3.1 Define the term solution. What kinds of solutions are possible? Write briefly about each kind of solution with an example.

3.2 Suppose a solid solution is formed between two substances, one whose particles are very large and the other whose particles are very small. What type of solid solution is this likely to be?

3.3 Define the following terms:
(i) Mole fraction (ii) Molality (iii) Molarity (iv) Mass percentage

3.4 Concentrated nitric acid used in the laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of solution is 1.504g mL^{-1}?

3.5 A solution of glucose in water is labelled as 10 percent w/w, what would be the molality and mole fraction of each component in the solution? If the density of the solution is 1.2g mL^{-1}, then what shall be the molarity of the solution?

3.6 How many mL of a 0.1M HCl are required to react completely with 1g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of two?

3.7 Calculate the percentage composition in terms of mass of a solution obtained by mixing 300g of a 25% and 400g of a 40% solution by mass.

3.8 An antifreeze solution is prepared from 222.6 g of ethylene glycol – $C_2H_4(OH)_2$, and 200g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL^{-1} then what shall be the molarity of the solution?

3.9 A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$, supposed to be carcinogen. The level of contamination was 15 ppm (by mass)
(i) Express this in percent by mass.
(ii) Determine the molality of chloroform in the water sample.

3.10 What role does the molecular interaction play in solution of alcohol and water?

3.11 Why do gases nearly always tend to be less soluble in liquids as the temperature is raised?

3.12 State Henry's law and mention some of its important applications?

3.13 The partial pressure of ethane over a saturated solution containing 6.56×10^{-2} g of ethane is 1 bar. If the solution contains 5.00×10^{-2}g of ethane, then what shall be the partial pressure of the gas.

3.14 What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{sol} H$ related to positive and negative deviations from Raoult's law?

3.15 An aqueous solution of 2 percent nonvolatile solute exerts a pressure of 1.004 bar at the boiling point of the solvent. What is the molecular mass of the solute?

3.16 Heptane and octane form ideal solution. At 373K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa, respectively. What will be the vapour pressure of a mixture of 25.0g of heptane and 35.0 g of octane?

3.17 The vapour pressure of water is 12.3 kPa at 300K. Calculate vapour pressure of 1 molal solution of a solute in it.

3.18 Calculate the mass of a nonvolatile solute (molecular mass 40) which should be dissolved in 114g octane to reduce its vapour pressure to 80%.

3.19 A solution containing 30g of a nonvolatile solute exactly in 90g water has a vapour pressure of 2.8 kPa at 298K. Further 18g of water is then added to solution, the new vapour pressure becomes 2.9 kPa at 298K. Calculate,
(i) Molecular mass of the solute (ii) vapour pressure of water at 298K.

3.20 A 5% solution (by mass) of cane sugar in water has freezing point of 271K. Calculate the freezing point of a 5% glucose in water if freezing point of pure water is 273.15K.

3.21 Two elements A and B form compounds having molecular formula AB_2 and AB_4. When dissolved in 20g of C_6H_6, 1g of AB_2 lowers the freezing point by 2.3K, whereas 1.0 g of AB_4 lowers it by 1.3K. The molar depression constant for benzene is 5.1 K kg mol^{-1} . Calculate atomic mass of A and B.

3.22 At 300 K, 36g of glucose present per litre in its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of solution is 1.52 bar at the same temperature., what would be its concentration?

UNIT 4

THERMODYNAMICS

OBJECTIVES

After studying this Unit, you will be able to:

- define spontaneous and non-spontaneous processes
- state second law of thermodynamics and apply the same for chemical and physical systems
- understand entropy as a measure of disorder and total entropy change as a criteria of spontaneity for chemical/physical changes
- state third law of thermodynamics
- establish relationship between
  - free energy change and spontaneity
  - free energy and useful work
  - free energy and equilibrium constant
- apply free energy change criteria in areas like metallurgy, biotechnology and biological processes

"The energy of the universe is constant; the entropy of the universe tends towards maximum."
- Rudolf Clausius

You have already studied in Class XI (Unit 5) that chemical and physical processes in a system are accompanied by energy changes. Such changes can be accounted for, by using the first law of thermodynamics. The essence of the first law is that all physical and chemical processes take place in such a manner that the total energy of the system and the surroundings is constant. The law has stood the test of time, as no transformation has been observed that violates the principle of conservation of energy. However, the first law is unable to answer the question, "*Why do transformations take place spontaneously in one direction but not in the other even though the energy is conserved in both the cases?*" Second law of thermodynamics answers this question. In this Unit, we shall develop the criteria for the spontaneity of a process. We have already discussed the *basic concepts* involved in thermodynamics in Unit-5 of Class XI. We shall use such concepts wherever necessary in this Unit.

4.1 SPONTANEOUS PROCESSES

We find that a cup of hot tea kept in a room cools spontaneously by losing heat to the surroundings. The first law of thermodynamics is obeyed because the energy lost by the system (i.e., the cup of hot tea) is gained by the surroundings. However, the first law will still be obeyed in the reverse process, namely, when the surroundings lose energy and the system gains it. We never observe such an amusing situation where a cup of tea at room temperature becomes hot on its own. In short, the cooling of a hot body in a room proceeds spontaneously but not its heating even though both processes are allowed by the first law.

Consider another example. If we add a drop of ink in a beaker containing water, the ink spreads spontaneously throughout the beaker making the whole solution coloured. Have you ever seen the reverse process where the dispersed ink spontaneously accumulates to form a single drop of ink? Similarly, two gases under the same pressure in two identical bulbs connected through a stopcock, mix and give a homogeneous mixture on opening the stopcock (Fig. 4.1). Contrary to this, we do not observe a mixture of two gases separating spontaneously in two pure gases each occupying one of the bulbs.

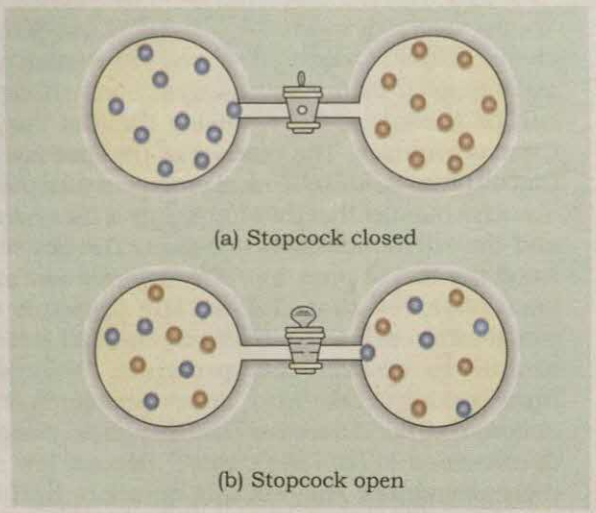


Fig. 4.1 *Spontaneous mixing of two gases (a) before mixing (b) after mixing.*

Now let us consider few examples involving chemical changes. We know that if equal volumes of equimolar solutions of hydrochloric acid and sodium hydroxide are mixed, the neutralization reaction proceeds spontaneously yielding sodium chloride and water. However, if sodium chloride is dissolved in water, the reverse reaction does not take place on its own.

In general, all transformations under given experimental conditions have a characteristic direction in which they proceed spontaneously; i.e., on their own without intervention of an outside agency. But what about the reverse process? We know that a cup of tea can be made hot by heating, but this is not a spontaneous process because an outside agency (a gas burner) has to be used. Similarly, an ink solution can be processed to obtain the ink drop; and two gases in a mixture can be separated if allowed to diffuse through a porous plug, and a solution of sodium chloride can be made to yield hydrochloric acid and sodium hydroxide. In each case, the change has to be brought about using some external agency. It does not take place on its own.

There is another feature of all spontaneous changes that may be noted. A cup of tea cools until it attains the temperature of the surroundings after which no further change in temperature is observed. We say that the cup of tea and the surroundings are in *thermal equilibrium*. The drop of ink similarly spreads until it is distributed uniformly. Mixing of two gases continues until each is evenly distributed throughout both the containers (Fig. 4.1). Thus we may conclude that **all spontaneous changes proceed till equilibrium is achieved**.

4.2 ENERGY AND SPONTANEITY

Common experience shows that **spontaneous processes involving macroscopic objects proceed with a decrease in potential energy.** A rock spontaneously rolls down a slope if it is dislodged, but it never rolls up to the top again

Expansion of an Ideal Gas into Vacuum

Expansion of an ideal gas through a pinhole into vacuum is a spontaneous process. In this expansion *there is no energy change of the system.* According to first law of thermodynamics, the gas can lose energy only in two ways. It can release heat to its surroundings or it can do work on them. In fig. 4.2 the gas chamber is insulated and there is no loss of heat to the surroundings (q = 0). Further, no work is done because no force is opposing expansion. For this isolated system, because $p_{ext} = 0$, it follows that $w = - p_{ext} \times \Delta V = 0$
Therefore, by first law of thermodynamics,
$\Delta U = q + w = 0 + 0 = 0$
Thus, **expansion of an ideal gas is an example of a spontaneous process in which there is no change of energy at all.**

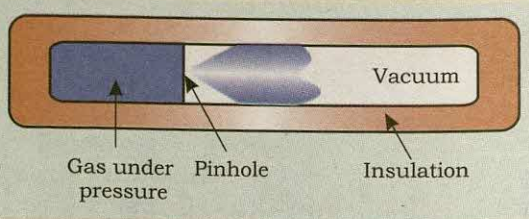
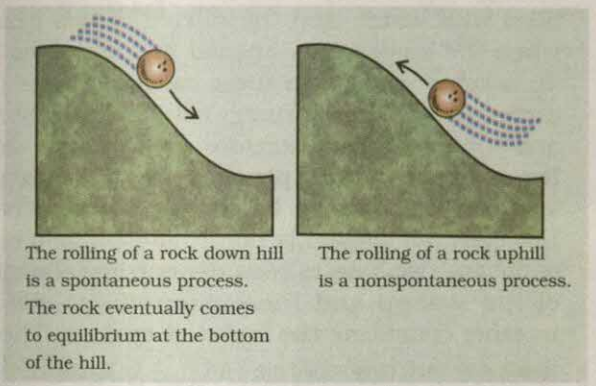


Fig. 4.2 *Spontaneous expansion of a gas into a vaccum.*

(Fig. 4.3). If you drop a bottle of glass, it falls spontaneously to the ground. When octane is ignited, it burns spontaneously in oxygen to give CO_2 and H_2O according to the reaction:



The rolling of a rock down hill is a spontaneous process. The rock eventually comes to equilibrium at the bottom of the hill.

The rolling of a rock uphill is a nonspontaneous process.

Fig. 4.3 *Examples of a spontaneous and non-spontaneous process.*

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l);$$
$$\Delta H^{\ominus} = -10951.3 \text{ kJ mol}^{-1}$$

Heat is evolved and the reaction is exothermic. Thus, we see that in the above example the system moves from a position of higher to lower energy. Now we may ask the question: Is it a general law of the nature that the process takes place in the direction of lower energy? The answer is no as we shall find in the following examples.

The evaporation of liquid water from an open beaker is spontaneous, but it is a process in which the system requires energy to evaporate water molecules. Dissolution of a solute in solvent is spontaneous even though the process may be endothermic i.e., it may require energy.

Dinitrogen pentoxide (N_2O_5) decomposes spontaneously at room temperature into NO_2 and O_2 although the reaction is endothermic

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g);$$
$$\Delta H^{\ominus} = 219.0 \text{ kJ mol}^{-1}$$

Similarly, the reaction between barium hydroxide and ammonium thiocyanate is highly endothermic:

$$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4SCN(s) \rightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l),\ \Delta H = +ve$$

Experience tells us that highly exothermic processes are generally spontaneous but some endothermic processes may also be spontaneous showing that lowering of energy is not the only determining factor for spontaneity. We shall now try to explore the missing factor which may lead us to a definite answer.

4.3 DISORDER, ENTROPY AND SECOND LAW OF THERMODYNAMICS

We may note that during the spontaneous evaporation of water, there is increase in the energy of the molecules and the process is endothermic. However, this leads to greater disorder amongst water molecules in the vapour states compared to the liquid state. The disorder is the manifestation of another thermodynamic property called **entropy** and is represented by the symbol(*S*). Obviously, entropy, like any other thermodynamic property such as internal energy (*U*) and enthalpy(*H*) should be a state function. The entropy change, ΔS is given by the equation

$$\Delta S = \frac{q_{rev}}{T} \qquad (4.1)$$

Here, q_{rev} is the heat absorbed when the process is carried out reversibly and isothermally (i.e., at constant *T*). If q is expressed in joule (J) and temperature in kelvin (K), then entropy change is given in unit of J/K or JK^{-1}. The ΔS is independent of path, therefore, it is a state function.

q_{rev}/T is a measure of increase in disorder of the system. This can be justified on the grounds that the absorption of heat into a system leads to the vigorous movement of the molecules due to increased kinetic energy. In other words, the more heat the system absorbs, the more disordered it becomes. Furthermore, if heat is absorbed at low temperature it becomes more disordered than when the same amount of heat is added at higher temperature. This is obvious as *T* is placed in denominator in Eq. (4.1).

Now we would like to use entropy changes for formulating rule for determining the direction of spontaneity of a process. Search for answer to this question leads us to the second law of thermodynamics. The second law of thermodynamics like the first law is a matter of experience. Like the first law there are several ways of stating the second law of thermodynamics.

A useful form of the second law is that *for a spontaneous process in an isolated system, the change in entropy is positive.* We already know that for an isolated system, energy remains constant. Therefore, increase in entropy in such a system is the natural direction of a spontaneous change.

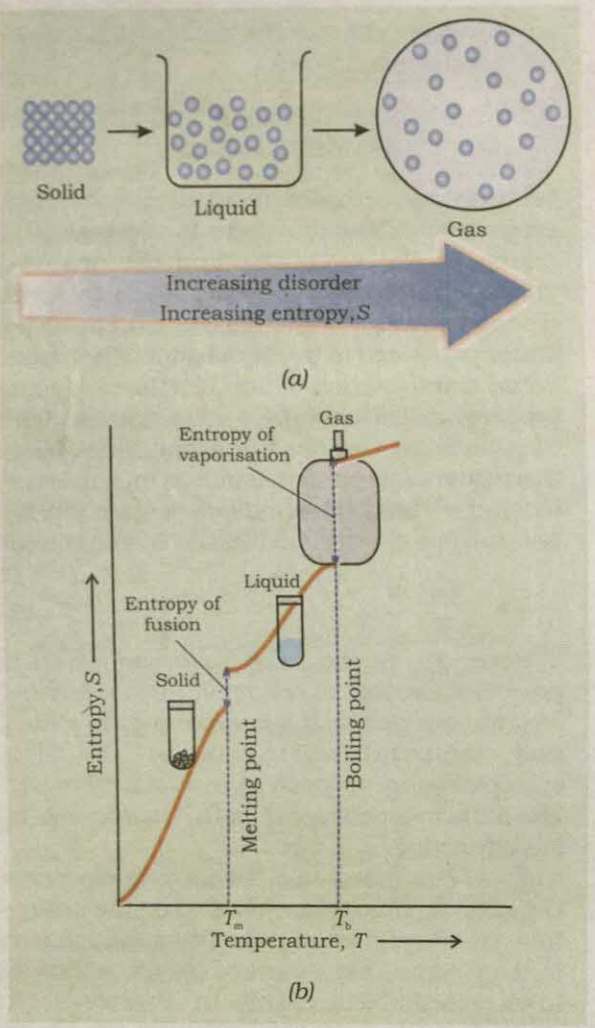


Fig. 4.4 *(a) As a sample changes from solid to liquid to gas, its particles become increasingly less ordered, and its entropy increases.*
(b) The entropy of a solid increases as its temperature is raised. The entropy increases sharply when the solid melts to form the more disordered liquid and then gradually increases again up to the boiling point. A second larger jump in entropy occurs when the liquid turns into vapour.

To form a mental picture, one can think of entropy as a measure of the degree of randomness or disorder in the system. The greater the disorder in such an isolated system, the higher is the entropy. For a given substance, the crystalline solid state is the state of lowest entropy (most ordered); the gaseous state is the state of highest entropy, and the liquid state is intermediate between the two. It is obvious that at a given temperature a gas is more disordered than liquid and a liquid is more disordered than a solid (Fig. 4.4).

Let us further illustrate the concept of entropy. Spreading of an ink droplet in a beaker filled with water, and the mixing of two gases when the stopcock is opened are examples of an isolated system. In these cases, there is no exchange of matter or energy between the system and surroundings. Therefore, we can state that **for a spontaneous process in an isolated system, the change in entropy is positive.** However, if a system is not isolated, e.g. 'a cup of hot tea', we have to consider entropy changes of the system and the surroundings which together constitute **the isolated system.** Thus, the total entropy change (ΔS_{total}) is sum of the change in entropy of the system (ΔS_{system}) and the change in entropy of the surroundings ($\Delta S_{surroundings}$) i.e.,

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \quad (4.2)$$

For a spontaneous process ΔS_{total} must be positive, i.e.,

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0 \quad (4.3)$$

When an isolated system is in equilibrium, the entropy is maximum. The mathematical condition for entropy (S) to be maximum is that the change in entropy(ΔS) is zero, i.e.,

$$\Delta S = 0 \text{ (at equilibrium for an isolated system)} \quad (4.4)$$

This can be illustrated if we consider the entropy changes in the conversion of water to ice at three different temperatures. The relevant entropy changes for the system, surrounding and total change are given in Table 4.1. We find that at 272 K, freezing is spontaneous because ΔS_{total} is positive. At 274K, ΔS_{total} is negative and freezing is not spontaneous but the reverse change, i.e., melting is spontaneous. At 273K, ΔS_{total} is zero which means that neither freezing nor melting is spontaneous. At this temperature, water and ice are in equilibrium and no net change is observed. Thus we note that ΔS_{total} is a criterion for spontaneity of a change.

The second law of thermodynamics explains why spontaneous exothermic reactions are so common. In exothermic reactions, heat released by the reaction increases the disorder of the surroundings and overall entropy change is

Table 4.1 Entropy changes for the Transformation, $H_2O(l) \rightarrow H_2O(s)$ at 1 bar

Temperature °C	Temperature K	ΔS_{system} J/(K mol)	$\Delta S_{surroundings}$ J/(K mol)	ΔS_{total} J/(K mol)
- 1	272	- 21.85	+ 21.93	+ 0.08
0	273	- 21.99	+ 21.99	0
+ 1	274	- 22.13	+ 22.05	- 0.080

positive [Fig. 4.5(a)]. In some exothermic reactions, entropy of the system may also decrease due to conversion of a gas into a solid

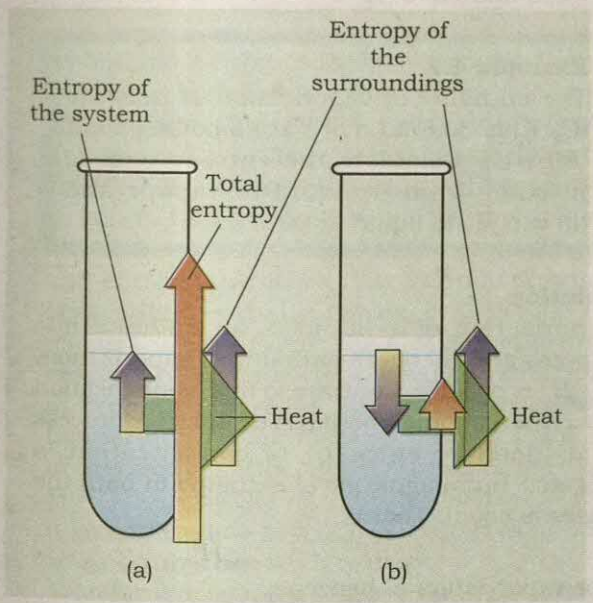


Fig. 4.5 *In an exothermic reaaction, (a) the overall entropy change is certainly positive when the entropy increases (b) The overall entropy change may also be positive when the entropy of the system decreases. The reactions are spontaneous in both the cases.*

product. However, if reaction is highly exothermic and increase in entropy of the surroundings is very high, the total entropy change will be positive and in such situation reaction will be spontaneous [Fig. 4.5(b)]. Let us take oxidation of magnesium which is highly exothermic. Conversion of oxygen into oxide results in decrease of entropy.

$2\,Mg\,(s) + O_2\,(g) \rightarrow 2MgO\,(s)$

$\Delta_r S^\ominus = -217\,J\,K^{-1}mol^{-1}$

$\Delta_r H^\ominus = -1202\,kJ\,mol^{-1}$

Heat released will increase the entropy of the surroundings and therefore

$$\Delta S^\ominus_{surr} = -\frac{(-1202\times10^3\,J\,mol^{-1})}{298\,K}$$

$$= +4.03\times10^3\,J\,K^{-1}\,mol^{-1}$$

$$\Delta S_{total} = -217\,J\,K^{-1}\,mol^{-1} + 4.03\times10^3\,J\,K^{-1}\,mol^{-1}$$

$$= +3.81\times10^3\,J\,K^{-1}\,mol^{-1}$$

Since ΔS_{total} is positive, reaction will be spontaneous.

In endothermic reactions, reactants on conversion into products go to higher energy state and temperature of the system falls. As a consequence, heat flows from surroundings into the system, the entropy of the surroundings decreases. If the disorder of the system rises sufficiently high and overall entropy increase is positive, the reaction will be spontaneous (Fig. 4.6).

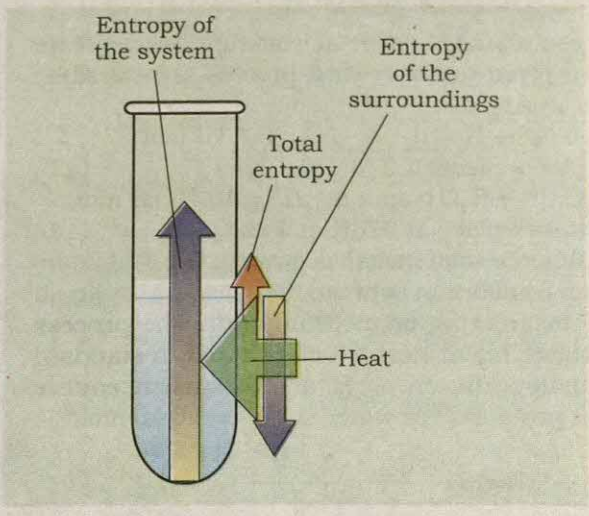


Fig. 4.6 *An endothermic reaction is spontaneous only if the entropy of the system increases enough to overcome the decrease in entropy of the surroundings.*

Example 4.1
Predict in which of the following, entropy increases/decreases:
(i) A liquid crystallizes into a solid.
(ii) Temperature of a crystalline solid is raised from 0 K to 115 K.
(iii) $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$
(iv) $H_2(g) \rightarrow 2H(g)$

Solution
(i) After crystallization molecules attain an ordered state and therefore, entropy decreases.
(ii) At 0 K, the nuclei of all atoms are static and entropy is minimum. If temperature is raised to 115 K, molecules begin to move and oscillate about their equilibrium positions in the lattice and system becomes more disordered, therefore entropy increases.
(iii) Reactant, $NaHCO_3$ is a solid and it has low entropy. Among products there are one solid and two gases. Therefore, the products represent a condition of higher entropy.
(iv) Here one molecule gives two atoms i.e., number of particles increases leading to more disordered state. Two moles of H atoms have higher entropy than one mole of hydrogen molecule.

4.4 ENTROPY CHANGE DURING PHASE TRANSFORMATIONS

Phase changes occur at constant temperature at a given pressure and process is reversible. For example,

$H_2O(s) \rightarrow H_2O(l)$; $\Delta_{fus}H^{\ominus} = 6.0$ kJ mol^{-1}
(takes place at 273K at 1 bar) (4.5)

$H_2O(l) \rightarrow H_2O(vap)$; $\Delta_{vap}H^{\ominus} = 40.79$ kJ mol^{-1}
(takes place at 373K at 1 bar) (4.6)

When a solid melts (as given in Eq. 4.5), there is an equilibrium between the solid and the liquid at the freezing or melting point. The process involves latent heat which is equal to standard enthalpy of fusion, $\Delta_{fus}H^{\ominus}$ at constant temperature and pressure. For water, $\Delta_{fus}H^{\ominus} = 6.0$ kJ mol^{-1}.

$$\Delta_{fus}S^{\ominus} = \frac{q_{rev}}{T} = \frac{\Delta_{fus}H^{\ominus}}{T}$$

$$= \frac{6.0\,\text{kJ mol}^{-1}}{273\,\text{K}} = \frac{6.0\times1000\,\text{J mol}^{-1}}{273\,\text{K}} = 21.99\ \text{J mol}^{-1}\text{K}^{-1}$$

Similarly, when a liquid is transformed into vapour at constant pressure and temperature,

$$\Delta_{vap}S^{\ominus} = \frac{\Delta_{vap}H^{\ominus}}{T}, \text{ (T is boiling point)}$$

Standard enthalpy of vaporization for water is 40.79 kJ mol^{-1}.

$$\Delta_{vap}S^{\ominus} = \frac{\Delta_{vap}H^{\ominus}}{T}$$

$$= \frac{40.79\,\text{kJ mol}^{-1}}{373\,\text{K}} = \frac{40.79\times1000\,\text{J mol}^{-1}}{373\,\text{K}}$$

$$= 109.356\ \text{J mol}^{-1}\text{K}^{-1}$$

Example 4.2
The enthalpy of vaporization of benzene (C_6H_6) is 30.8 kJ mol^{-1} at its boiling point (80.1°C). Calculate the entropy change in going from (i) liquid to vapour and (ii) vapour to liquid at 80.1°C.

Solution
Vaporization of a liquid is an endothermic process and therefore enthalpy of vaporization, $\Delta_{vap}H^{\ominus}$ is positive. Contrary to this, condensation (i.e., from vapour to liquid) is exothermic process and therefore enthalpy of condensation is negative but magnitude of enthalpy in both the cases is equal. That is,

$$\Delta_{vap}H^{\ominus} = -\Delta_{condens}H^{\ominus}$$

For vaporization of benzene,

$$\Delta_{vap}S^{\ominus} = \frac{\Delta_{vap}H^{\ominus}}{T}$$

$$= \frac{30.8\ \text{kJ mol}^{-1}}{353\,\text{K}} = \frac{30.8\times1000\,\text{J mol}^{-1}}{353\,\text{K}}$$

$$= 87.3\ \text{J K}^{-1}\,\text{mol}^{-1}$$

For condensation of benzene,

$$\Delta_{condens}S^{\ominus} = \frac{-\Delta_{vap}H^{\ominus}}{353\,K} = -87.3\ \text{JK}^{-1}\,\text{mol}^{-1}$$

4.5 ABSOLUTE ENTROPY

In this section we will investigate the effect of temperature on entropy of a substance. On increasing temperature of a substance translational, rotational and vibrational motions

Table 4.2 Standard molar entropies $S_m^\ominus$ /J K^{-1} mol^{-1} at 298 K

Solids	entropy	Liquids	entropy	Gases	entropy
C (graphite)	5.7	Hg	76.0	H_2	130.7
C(diamond)	2.4	H_2O	69.9	N_2	191.6
Fe	27.3	C_2H_5OH	160.7	O_2	205.1
Pb	64.8	C_6H_6	173.3	CO_2	213.7
Cu	33.1	CH_3COOH	159.8	NO_2	240.1
Al	96.2			N_2O_4	304.3
Fe_2O_3	87.4			NH_3	192.3
$CuSO_4.5H_2O$	300.4			CH_4	186.2
$C_{12}H_{22}O_{11}$(sucrose)	360.8				
CaO	39.8				
$CaCO_3$(calcite)	92.9				

become more vigorous leading to greater disorder and hence an increase in the entropy. Molecules of a substance undergo different types of motions-translational, rotational (molecule spin, like a top) and vibrational (when stretching and compression of bonds takes place). When temperature is increased, these motions become more vigorous and entropy increases. The entropy of a pure crystalline substance decreases as the temperature is lowered. As a matter of fact **the entropy of a perfectly crystalline substance approaches zero as the absolute zero of temperature is approached. This is third law of thermodynamics** which was enunciated in late 19th century by German chemist Walther Nernst. It gives base line from which entropies at other temperatures can be measured.

Molar entropy, the entropy per mole amount of a substance, is denoted by S_m. *Standard molar entropy*, the entropy per mole amount of substance in its standard state at the specified temperature is denoted by $S_m^\ominus$. The standard entropy of a substance or ion is also called *absolute entropy*. The definition of the entropy given by equation earlier helps in determination of entropy. The unit of molar entropy is J K^{-1} mol^{-1}.

Standard molar entropies of a few substances are given in Table 4.2 and in Appendix at the end of the book.

From the Table 4.2, you will find that standard molar entropy of gases at 1 bar pressure and 298K are all similar and are much larger than the standard molar entropies of most simple solids. This is because in a gas, the particles (with higher energies) are dispersed over a large volume. The table further shows that the standard molar entropies of liquids are intermediate between those of gases and solids.

4.5.1 Entropy Change For a Reaction

Entropy change for a chemical reaction (when reactants change completely into products) is calculated with the help of data given for standard molar entropies at a given temperature. From the sign of the entropy of a reaction, we can give qualitative information about the reaction. However, for quantitative work, we require standard entropy change, $\Delta_r S^\ominus$ for a reaction and it can be determined by subtracting the standard entropies of reactants from the standard entropies of products. Thus,

$$\Delta_r S_m^\ominus = \sum \nu_P S_m^\ominus(\text{products}) - \sum \nu_R S_m^\ominus(\text{reactants})$$

(ν_P and ν_R are stoichiometric coefficients)

For example, in a general reaction:

$aA + bB \rightarrow cC + dD$

$$\Delta_r S_m^\ominus = [c\,S_m^\ominus(C) + d\,S_m^\ominus(D)] - [a\,S_m^\ominus(A) + b\,S_m^\ominus(B)]$$

For oxidation of iron, $4Fe(s)+3O_2(g) \rightarrow 2Fe_2O_3(s)$ using Table 4.2, we can write

$$\Delta_r S_m^\ominus = 2S_m^\ominus(Fe_2O_3) - \left[4 \times S_m^\ominus(Fe) + 3 \times S_m^\ominus(O_2)\right]$$

$$= \{2 \times 87.4 - (4 \times 27.3 + 3 \times 205.0)\}\text{J K}^{-1}\text{ mol}^{-1}$$

$$= -549.4\text{ J K}^{-1}\text{ mol}^{-1}$$

As expected, there is a large decrease in entropy during the reaction, mostly because the highly dispersed oxygen gas reacts to form the compact solid Fe_2O_3. Now, we would like to

understand that inspite of the negative entropy of the reaction, why is the reaction spontaneous. As already emphasised, ΔS_{total}(ΔS_{System} + $\Delta S_{Surroundings}$) only decides the spontaneity of a reaction. In this case, heat evolved during the reaction increases the entropy of the surroundings.

For calculating entropy changes in the surroundings, we have to consider the heat absorbed by the surroundings which is equal to $-\Delta_r H^\ominus$. At temperature T, the entropy change of the *surroundings* is

$$\Delta S_{(surroundings)} = \frac{q}{T} = -\frac{\Delta_r H^{\theta 1}}{T} \qquad (4.7)$$

In Eq. (4.7), because $-\Delta_r H^\ominus$ is positive and so $\Delta_r S^\ominus$ (surroundings) is also positive, corresponding to an increase from its initial value.

$$\Delta S^\ominus_{(surroundings)} = \frac{-(-1648\times10^3\ J\ mol^{-1})}{298\ K}$$

($\Delta_r H^\ominus$ for the reaction is -1648×10^3 J mol^{-1})

$$= 5530\ J\ K^{-1}mol^{-1}$$

This high increase in entropy of the surroundings is due to release of energy (heat) into surroundings.

Thus, total entropy change for the oxidation of iron,

$$\Delta_r S^\theta_{m\ (total)} = \Delta_r S^\theta_{(surroundings)} + \Delta_r S^\theta_{(system)}$$

$$= -\Delta_r H^\ominus / T + \Delta_r S^\ominus_{(system)}$$

$$= (+5530\ J\ K^{-1}mol^{-1}) + (-549.4\ J\ K^{-1}mol^{-1})$$

$$= +4980.6\ J\ K^{-1}mol^{-1}$$

This overall increase in the entropy makes the oxidation of iron 4Fe (s) + $3O_2$ (g) $\rightarrow$ $2Fe_2O_3$ (s) spontaneous.

Example 4.3

Calculate the change of entropy, $\Delta_r S^\ominus$ at 298K for the reaction in which urea is formed from NH_3 and CO_2.

$2NH_3(g) + CO_2(g) \rightarrow NH_2CONH_2(aq) + H_2O(l)$

The standard entropy of NH_2CONH_2 is 174.0 J $K^{-1}mol^{-1}$.

Solution

Using Table 4.2 for the entropy values of other components:

$$\Delta_r S^\ominus_m = \sum v_P S^\ominus (products) - \sum v_R S^\ominus (reactants)$$

$$= [(174.0 + 69.9) - (2\times192.3 + 213.7)]\ JK^{-1}mol^{-1}$$

$$= (243.9 - 598.3)\ J\ K^{-1}mol^{-1} = -354.4\ J\ K^{-1}mol^{-1}$$

Here, sign of the entropy change $\Delta_r S^\ominus$ is according to expectation. By examining the equation for formation of urea from ammonia and carbon dioxide, we find that there is decrease in the number of moles when reactants are converted into products. Secondly, reactants go from gaseous state to aqueous/liquid state which also favours decrease in entropy.

4.6 GIBBS ENERGY AND SPONTANEITY

We have seen that for a system which is not isolated from its surroundings, it is the total entropy change, ΔS_{total} which decides the spontaneity of the process.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

In our analysis for the reaction of oxidation of iron, we found that $\Delta S_{surroundings}$ could be calculated from the knowledge of $\Delta H_{surroundings}$ and T; that is

$$\Delta S_{surroundings} = \Delta H_{surroundings} / T = -\Delta H_{system}/T$$

Therefore,

$$\Delta S_{system} + \left(-\frac{\Delta H_{system}}{T}\right) = \Delta S_{total}$$

If we multiply this equation throughout by T, we have

$$T\Delta S_{system} + (-\Delta H_{system}) = T\Delta S_{total}$$

or $$\Delta H_{system} - T\Delta S_{system} = -T\Delta S_{total} \qquad (4.8)$$

The Eq. (4.8) is so important and so useful as a manifestation of the second law that a new thermodynamic function, the **Gibbs energy or Gibbs function, G,** has been defined as $G = H - TS$. **(In earlier literature this was called Gibbs free energy but in accordance with IUPAC recommendations we shall use the term Gibbs energy.)** Therefore, the change in Gibbs energy for the system, ΔG_{system} is

$$\Delta G_{system} = \Delta H_{system} - T\Delta S_{system} - S_{system}\Delta T,$$

[1] By definition, in general, $\Delta S = \frac{q_{rev}}{T}$, but for a process at constant pressure; $q = q_p = \Delta H$. Therefore, $\Delta S = \frac{\Delta H}{T}$.

At constant temperature, $\Delta T=0$

$$\therefore \Delta G_{system} = \Delta H_{system} - T\Delta S_{system} \quad (4.9)$$

Usually the subscript 'system' is dropped and we simply write this equation as

$$\Delta G = \Delta H - T\Delta S \quad (4.10)$$

Thus, Gibbs energy change = enthalpy change – temperature × entropy change, and is referred to as the **Gibbs energy equation**, one of the most important equations in chemistry. Here we have considered both terms together for spontaneity: energy (in terms of ΔH) and entropy, ΔS (a measure of disorder) as indicated earlier in this Unit. Dimensionally if we analyse, we find that ΔG has units of energy because both ΔH and the $T\Delta S$ are energy terms [Since $T\Delta S$ = (K)J/(K mol) = J/mol or J mol^{-1}].

Now let us consider how ΔG is related to reaction spontaneity from Eq. (4.11) obtained by combining Eq. (4.8) and (4.9) i.e.,

$$\Delta G_{system} = - T\Delta S_{total} \quad (4.11)$$

The second law states that ΔS_{total} increases (ΔS_{total} is positive) in a spontaneous process, and so it follows that G_{system} should decrease i.e. ΔG_{system} should have a negative value in a spontaneous process.

Let us now state criteria of spontaneity based at constant temperature and pressure on Eq. (4.11).

(i) **if ΔG_{system} is negative (<0), the process is spontaneous.**

(ii) **if ΔG_{system} is positive (>0), the process is not spontaneous.**

(iii) **if ΔG_{system} = 0, the sytem has attained equilibrium with respect to the transfromation.**

4.6.1 Gibbs Energy of Reaction and the Standard Gibbs Energy of Formation

We have seen that enthalpy and entropy changes can be calculated for chemical reactions by using values of $\Delta_f H^\ominus$ and $S^\ominus$ for the substances in the reaction. $\Delta_r G^\ominus$ can be found from the resulting values of $\Delta_f H^\ominus$ and $S^\ominus$ using Eq. (4.10). Let us illustrate with the help of the following example.

Example 4.4

Calculate the standard Gibbs energy change for the formation of methane at 298K.

$C_{(graphite)} + 2H_2(g) \rightarrow CH_4(g)$

J. Willard Gibbs

J. Willard Gibbs, a Professor of Mathematical physics at Yale University, USA from 1871 till his death in 1903, introduced the concept of free energy into chemical thermodynamics. He was the first person to show how the laws of thermodynamics apply to chemical processes. His outstanding contributions to chemical thermodynamics could not be recognised until 13 years as he published his work in some obsecure journals. Gibbs work got recognition when his work was translated into French and German. To commemorate Gibbs, free energy was given the symbol G. IUPAC has now recommended that Gibbs free energy should be used only as *'Gibbs energy'*.

Solution

Let us first consider values of $\Delta_f H^\ominus$ and $S^\ominus$ from the table given earlier (in Class XI) and in the Table 4.2.

	$C_{(graphite)}$	$H_2(g)$	$CH_4(g)$
$\Delta_f H^\ominus$ /k J mol^{-1}	0	0	-74.81
$S_m^\ominus$ /$JK^{-1}mol^{-1}$	5.70	130.7	186.3

Now using the above data

$\Delta_r H^\ominus = \Delta_f H^\ominus\ CH_4(g) - \{\Delta_f H^\ominus C_{(graphite)} + 2\Delta_f H^\ominus\ H_2(g)\}$

$= -74.81\ kJ\ mol^{-1} - (0 + 0)$

$= -74.81\ kJ\ mol^{-1}$

$\Delta_r S_m^\ominus = S_m^\ominus\ CH_4\ (g) - \{ S_m^\ominus\ C_{(graphite)} + 2S_m^\ominus\ H_2(g)\}$

$= [1(186.3\ JK^{-1}mol^{-1}] - [1(5.70\ JK^{-1}\ mol^{-1}) + 2\ (130.7\ J\ K^{-1}mol^{-1})]$

$= -80.8\ JK^{-1}\ mol^{-1}$

Substituting the values of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ in Gibbs equation, we get

$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$

$= -74.81\ kJ\ mol^{-1} - (298K)(-80.8\times10^{-3}kJ\ K^{-1}mol^{-1})$

$= -74.81\ kJ\ mol^{-1} + 24.1\ kJ\ mol^{-1} = -50.7\ kJ\ mol^{-1}$

In this case, value of Gibbs energy is negative and therefore reaction is spontaneous. Further, this example illustrates how standard Gibbs energy change can be calculated for the formation of one mole of a compound from its elements, with all reactants and products in their standard states at a specified temperature. Here in this example, the calculated $\Delta_r G^\ominus$ can be identified as the *standard molar* Gibbs energy of formation for methane, $\Delta_f G^\ominus[CH_4(g)]$. The

Table 4.3 Standard Gibbs energy of formation, $\Delta_f G^\ominus$ / kJ mol^{-1} at 298 K

Solid Compounds	$\Delta_f G^\ominus$	Simple gaseous molecules	$\Delta_f G^\ominus$
BaO	–528.4	HCl	–95.27
$BaCO_3$	–1139	H_2O	–228.6
$BaSO_4$	–1465	H_2O_2	–103.3
CaO	– 604.2	CO	–137.3
$Ca(OH)_2$	– 896.6	CO_2	–394.4
$CaCO_3$	–1129	SO_2	–300.4
CuO	–127	SO_3	–370.4
NaCl	– 384.0	NO_2	51.84
KCl	– 408.3	N_2O	104
NH_4Cl	– 203.0	NH_3	–16.6
Al_2O_3	–1582.4	O_3	163.4
Fe_2O_3	–741.0	NO	86.69
ZnO	– 318.2	CH_4	–50.79
SiO_2	– 805	C_2H_6 (ethane)	229
PbO_2	– 219	C_3H_8 (propane)	270
		C_4H_{10} (*n* – butane)	310
Liquids		C_4H_{10} (*iso* – butane)	310
CH_3OH	–166.2	C_2H_2 (acetylene)	209.2
C_2H_5OH	–174.8	C_2H_4 (ethylene)	219.4
C_6H_6	–124.5	C_3H_6 (propylene)	266.9
CH_3COOH	– 392	C_4H_8 (1– butene)	307.4
H_2O	– 237.2	C_4H_8 (*cis* - 2 - butene)	301
H_2O_2	–120.4	C_4H_8 (*trans* - 2 - butane)	297
HCl (aq)	–131.3	C_4H_8 (*iso* – butene)	294

values of $\Delta_f G^\ominus$ for some compounds are listed in Table 4.3 and for more substances, values are given in the Appendix at the end of this book. From the table you can see that values of $\Delta_f G^\ominus$ for elements are zero as in case of $\Delta_f H^\ominus$.

Similar to standard enthalpies of formation, we can make use of $\Delta_f G^\ominus$ data for calculating Gibbs energy of a reaction $\Delta_r G^\ominus$, we may write the equation as follows:

$$\Delta_r G^\ominus = \Sigma v_P \Delta_f G^\ominus \text{ (products)} - \Sigma v_R \Delta_f G^\ominus \text{ (reactants)} \quad (4.12)$$

Example 4.5

Silane, SiH_4 like methane, burns in air. The product silica (silicon oxide) is solid quite unlike carbon dioxide.

SiH_4 (g) + $2O_2$(g) → SiO_2 (s) + $2H_2O$ (g)

Standard Gibbs energy of formation of SiH_4 (g) is +52.3 kJ mol^{-1}. Values for SiO_2 and H_2O can be taken from Table 4.3. Calculate the value of $\Delta_r G^\ominus$.

Solution

Applying Eq. (4.12)

$\Delta_r G^\ominus = \Sigma \nu_P \Delta_f G^\ominus$ (products) $- \Sigma \nu_R \Delta_f G^\ominus$ (reactants)

$= \left[\Delta_f G^\ominus (SiO_2) + 2\Delta_f G^\ominus (H_2O)\right] -$

$\left[\Delta_f G^\ominus (SiH_4) + 2\Delta_f G^\ominus (O_2)\right]$

Gibbs energy of formation of elements being zero, we have

$\Delta_r G^\ominus = [-(805 \text{ kJ mol}^{-1}) + 2 (-228.6 \text{ kJ mol}^{-1})] -$
$[1(+52.3 \text{ kJ mol}^{-1}) + 0]$

$= [-1262.2 \text{ kJ mol}^{-1}] - [52.3 \text{ kJ mol}^{-1}]$

$= -1314.5 \text{ kJ mol}^{-1}$

Negative value of $\Delta_r G^\ominus$ supports spontaneity of the above reaction.

4.6.2 Gibbs energy, Temperature and Spontaneity

We have just observed that spontaneity of a chemical reaction is decided by two factors taken together: (i) the enthalpy (energy) factor, and (ii) the entropy factor.

The equation, $\Delta G = \Delta H - T\Delta S$, takes both the factors into consideration. ΔG is negative when ΔH is negative while ΔS is positive. For example, in combustion of carbon at 298 K,

$C_{(graphite)} + O_2(g) \rightarrow CO_2$ (g); $\Delta_r H^\ominus = -393.5 \text{ kJ mol}^{-1}$, $\Delta_r S^\ominus = 0.0029 \text{ kJ K}^{-1} \text{ mol}^{-1}$ and, therefore, $\Delta_r G^\ominus = -394.4 \text{ kJ mol}^{-1}$, the reaction is spontaneous.

In case ΔH and ΔS are both negative, and if magnitude of ΔH is very high, ΔG will be negative and here we say reaction is *enthalpy driven*. For example, in combustion of methane,

CH_4 (g) + $2O_2$ (g) $\rightarrow 2H_2O$ (l) + CO_2 (g);

$\Delta_r H^\ominus = -890.3 \text{ kJ mol}^{-1}$,

$\Delta_r S^\ominus = -0.2430 \text{ kJ K}^{-1} \text{ mol}^{-1}$ and

$\Delta_r G^\ominus = -817.9 \text{ kJ mol}^{-1}$

If a reaction has a positive enthalpy change and positive entropy change, the only way it can be spontaneous is if $-T\Delta S$ is large enough to outweigh ΔH. This can happen in two ways: (a) The positive entropy change of the system can be 'small' in which case T must be large (b) The positive entropy change of the system can be 'large', in which case T may be small. The former is one of the reasons why reactions are often carried out at high temperature. In either case, the reaction is entropy driven. Now we shall find the effect of temperature on value of $\Delta_r G^\ominus$. Here we assume that $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ are constant over a reasonable range of temperature.

Let us take the example of manufacture of iron. Iron can be obtained from its oxide ore, Fe_2O_3. Is it possible to get iron by simply heating Fe_2O_3 and decomposing the oxide into iron and oxygen?

$$Fe_2O_3 \text{ (s)} \rightarrow 2Fe \text{ (s)} + 3/2\ O_2 \text{ (g)}$$

Feasibility of the reaction can be predicted on the basis of the value of $\Delta_r G^\ominus$. At room temperature $\Delta_r H^\ominus$ (+ 824 kJmol^{-1}) is unfavourable and $\Delta_r S^\ominus$ (+ 0.276 kJ K^{-1} mol^{-1}) is favourable. Unfortunately, $\Delta_r H^\ominus$ has large positive value and it cannot be outweighed by $-T\Delta_r S^\ominus$ (= – 82kJ at 298K) at any reasonable temperature. The value of $\Delta_r G^\ominus$ at 298K is +742 kJ mol^{-1}.

The usual method of reducing Fe_2O_3 to iron is to use carbon, the cheapest reducing agent. The decomposition of iron oxide which is nonspontaneous is compensated by highly spontaneous process of combustion of carbon, $C_{(graphite)} + O_2(g) \rightarrow CO_2$ (g)

The overall process can be represented by

2 Fe_2O_3 (s) + 3 C (s) $\rightarrow$ 4 Fe (s) + 3 CO_2 (g)

Although entropy change is positive, the $-T\Delta_r S^\ominus$ (= −187 kJ) is not large enough to counter the positive enthalpy change at 298K). However, at higher temperature the contribution of $-T\Delta_r S^\ominus$ becomes more negative and finally overtakes the positive enthalpy change. Let us calculate temperature, T at which $\Delta_r G^\ominus$ is zero from the equation.

$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$, substituting the values of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$,

$0 = +467.9 \text{ kJ mol}^{-1} - T\ (0.5603 \text{ kJ mol}^{-1} \text{ K}^{-1})$

$T = 835.1$ K (or 561.9°C ≈ 562°C)

The free energy change for the reaction becomes zero at 562°C, and at higher temperature it will be negative. Therefore, for achieving the spontaneity, temperature of the furnace in iron metallurgy is kept sufficiently high (much higher than 562°C).

Table 4.4 summarises our discussion in the preceding pages.

Example 4.6

Find out whether it is possible to reduce MgO using carbon at 298K. If not, at what temperature it becomes spontaneous. For reaction, MgO (s) + C (s) $\rightarrow$ Mg (s) + CO (g), $\Delta_r H^\ominus = +491.18 \text{ kJ mol}^{-1}$ and $\Delta_r S^\ominus = 197.67 \text{ JK}^{-1} \text{ mol}^{-1}$.

Table 4.4 Effect of temperature on Spontaneity of reactions

$\Delta_r H^\ominus$	$\Delta_r S^\ominus$	$\Delta_r G^\ominus$	*Description**
–	+	–	Reaction spontaneous at all temperatures
+	–	+	Nonspontaneous at all temperatures
–	–	– (at low T)	Reaction spontaneous at low temperature
		+ (at high T)	Reaction nonspontaneous at high temperature
+	+	+ (at low T)	Reaction nonspontaneous at low temperature
		– (at high T)	Reaction spontaneous at high temperature
+	–	+ (at all T)	Reaction nonspontaneous at all temperatures

* The term low temperature and high temperature are relative. For a particular reaction, high temperature could even mean room temperature.

Solution

We know, $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$

$= +491.18\ \text{kJmol}^{-1} - (298\text{K})(0.198\ \text{kJK}^{-1}\text{mol}^{-1})$

$= +491.18\ \text{kJmol}^{-1} - 59.00\ \text{kJ mol}^{-1}$

$= 432.18\ \text{kJ mol}^{-1}$

Free energy change is positive, therefore, at 298 K reduction is not possible.

Temperature T, at which $\Delta_r G^\ominus = 0$,

$$T = \Delta_r H^\ominus / \Delta_r S^\ominus = \frac{491.18\ \text{kJ mol}^{-1}}{0.198\ \text{kJ mol}^{-1}\text{K}^{-1}}$$

$$= 2480.7\ \text{K}$$

Therefore, the reaction will be spontaneous above 2480.7K (or above 2207.7° C). Hence this high temperature does not permit commercial use of this process.

4.6.3 Gibbs Energy and Work

We have just seen that ΔG is a measure of the spontaneity of a chemical reaction. This property is very useful to chemists. There is another aspect of Gibbs energy change which is based on its relationship to *useful work* other than pressure-volume work that is obtainable from the system. It can be shown that Gibbs energy for a process is equal to the maximum possible useful work that can be derived from the process, i.e.,

$$\Delta G = w_{max} \quad (4.13)$$

(for a reversible change at constant T, P)

Thus, in principle , any process that occurs spontaneously can be utilised for performance of work. The greater the Gibbs energy change, the greater is the amount of work that can be obtained from the process.

Let us consider the glucose metabolism in our body. When 1 mol of glucose is oxidised,

$\Delta H^\ominus = -2808\ \text{kJ mol}^{-1}$ and

$\Delta G^\ominus = -2870\ \text{kJ mol}^{-1}$

Thus, the maximum amount of work that can be done by a person as a result of metabolising 1 mol (180.2g) of glucose is 2870 kJ. Suppose a man (mass 60 kg) climbs a height of 100 metres, he would need to do $60\ \text{kg} \times 9.8\ \text{m s}^{-2} \times 100\ \text{m} = 58800\ \text{J} = 58.8\ \text{kJ}$ of work (we know that w = mgh). In order to do this work, he would need to metabolise a minimum of (180.2 g/2870 kJ) (58.8 kJ) = 3.7 g of glucose. In practice, the conversion of energy to work in the body is not 100 percent efficient; he would, therefore, need more than 3.7 g of glucose.

In case of galvanic cells (Unit 5), Gibbs energy change, ΔG, is related to the electrical work done by the cell. If E is the e.m.f. of the cell and n mole of electrons are involved, the electrical work will be equal to nFE (where F is the Faraday constant). Thus,

$$\Delta_r G = -nFE_{cell}$$

If reactants and products are in their standard states

$$\Delta_r G^\ominus = -nFE^\ominus_{cell}$$

Here, $E^\ominus_{cell}$ is the standard cell potential.

4.6.4 Coupled Reactions

There are reactions for which the value of $\Delta_r G$ is not negative i.e., they are nonspontaneous. However, such reactions can be made spontaneous if these are coupled (means

carrying both reactions simultaneously) with reactions having a very large negative Gibbs energy of reaction. Let us consider the decomposition of iron oxide, Fe_2O_3 into iron.

$2Fe_2O_3(s) \rightarrow 4Fe(s) + 3O_2(g)$;

$\Delta_r G^\ominus = +1487.0\ kJmol^{-1}$ (a)

Positive $\Delta_r G^\ominus$ shows that the reaction is nonspontaneous. This can be achieved by coupling decomposition of Fe_2O_3 with a reaction having a highly negative $\Delta_r G^\ominus$.

Let us consider the reaction

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$;

$\Delta_r G^\ominus = -514.4\ kJmol^{-1}$ (b)

In equation (a) 3 mol of O_2 is involved. Therefore, we can write equation (b) as

$6CO(g) + 3O_2(g) \rightarrow 6CO_2(g)$;

$\Delta_r G^\ominus = -1543.2\ kJmol^{-1}$ (c)

(Please remember in all these cases the symbol 'per mole' or mol^{-1} is used which means-per mole of balanced chemical equation as discussed in Class XI, Unit 5).

Let us add equation (a) and (c)

$2Fe_2O_3(s) \rightarrow 4Fe(s) + 3O_2(g)$; $\Delta_r G^\ominus = +1487\ kJ\ mol^{-1}$

$6CO(g) + 3O_2(g) \rightarrow 6CO_2(g)$; $\Delta_r G^\ominus = -1543.2\ kJ\ mol^{-1}$

$2Fe_2O_3(s) + 6CO(g) \rightarrow 4Fe(s) + 6CO_2(g)$;

$\Delta_r G^\ominus = -56.2\ kJ\ mol^{-1}$

Negative value of $\Delta_r G^\ominus$ indicates that iron(III) oxide can be reduced spontaneously to free iron with carbon monoxide. In fact, this is the reaction which takes place in the lower part of blast furnace where iron ore is reduced to iron. This concept of coupling two reactions(one spontaneous and one nonspontaneous) is very useful in biological systems (Unit 17). Adenosine triphosphate, or ATP, is a large molecule containing phosphate groups. When ATP reacts with water in presence of an enzyme, it is hydrolysed to give adenosine diphosphate, ADP, and a phosphate ion.

$ATP + H_2O \rightarrow ADP + \text{phosphate ion}$;

$\Delta_r G^\ominus = -31\ kJ\ mol^{-1}$

This reaction is coupled to various non-spontaneous reactions to carry out the necessary reactions in biological systems. For example, the biosynthesis of sucrose from glucose and fructose has a $\Delta_r G^\ominus$ of +23 kJ mol^{-1}. Hence, this reaction can be driven by the hydrolysis of ATP.

Glucose + Fructose + ATP $\rightarrow$ Sucrose + ADP ;

$\Delta_r G^\ominus = -8\ kJ\ mol^{-1}$

4.7 GIBBS ENERGY CHANGE AND EQUILIBRIUM CONSTANT

We have seen that for a chemical reaction to occur, Gibbs energy change should be negative. During the course of a reaction, Gibbs energy decreases and composition of reaction mixture changes with time and finally a constant composition of the mixture is obtained. A curve of the shape ∪ (shown in Fig. 4.7) is obtained.

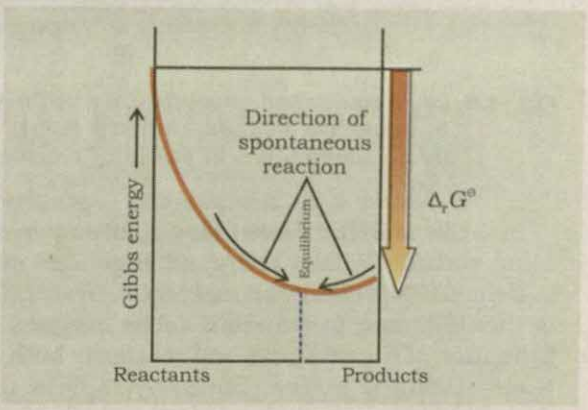


Fig. 4.7 *At constant temperature and pressure, the direction of spontaneous change is towards lower Gibbs energy. The equilibrium composition of a reaction mixture corresponds to the lowest point on the curve. In this example, substantial quantities of both reactants and products are present at equilibrium and K is close to 1.*

The composition at lowest point of the curve – point of minimum Gibbs energy – corresponds to **equilibrium**. For a system at equilibrium, any change (either the forward or reverse reaction) would lead to an increase in Gibbs energy and therefore neither change is spontaneous once the system attains equilibrium. When minimum Gibbs energy lies very close to the products, the equilibrium composition strongly favours products and reaction goes near to completion. When minimum Gibbs energy lies very close to the reactants, the equilibrium composition favours the reactants and reaction '*does not go*'. Both the situations are shown below in Fig. 4.8 (a and b).

Sometimes, minimum value lies approximately halfway between products and reactants and in such situations, both reactants and products are in similar abundance and equilibrium constant, *K* is close to 1.

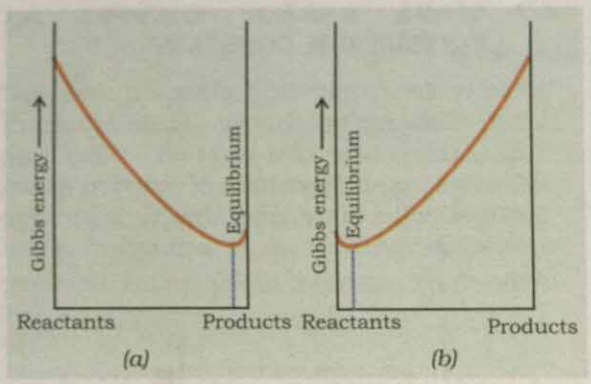


Fig. 4.8 *(a) At equilibrium, products are much more in abundance than the reactants (K>>1). (b) Equilibrium lies in favour of reactants (K<<1).*

In order to make these ideas quantitative we must consider Gibbs energy change, $\Delta_r G$ and standard Gibbs energy change, $\Delta_r G^\ominus$. Here, $\Delta_r G^\ominus$ is the difference in standard Gibbs energies of formation of the products and reactants both in their standard states. Similarly, $\Delta_r G$ is the reaction Gibbs energy change at a definite, fixed composition of the reaction mixture. Let us consider formation of ammonia where nitrogen and hydrogen are reactants.

The Gibbs energy of reaction, $\Delta_r G$, is related to the composition of the reaction mixture and to standard reaction Gibbs energy, $\Delta_r G^\ominus$ by the equation:

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$$

where Q is the reaction quotient and R is the gas constant, with the value 8.314 $JK^{-1}mol^{-1}$. If the species are gases, these concentrations are expressed in partial pressure and reaction quotient will be Q_p and if species are in solution, reaction quotient will be expressed in terms of molar concentration as Q_c.

At equilibrium, $Q = K$ and therefore, above equation becomes

$$0 = \Delta_r G^\ominus + RT \ln K$$

or $$\Delta_r G^\ominus = - RT \ln K$$

or $$\Delta_r G^\ominus = - 2.303\ RT \log K \qquad (4.14)$$

The Eq. (4.14) can also be written as

$$K = e^{-\Delta_r G^\ominus / RT} = 10^{-\Delta_r G^\ominus / 2.303 RT}$$

We also know that

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = - RT \ln K$$

Since $\Delta_r G^\ominus$ depends on the value of $\Delta_r H^\ominus$, for strongly endothermic reactions the value of $\Delta_r H^\ominus$ may be large and positive. In such case, value of K will be much smaller than 1 and the reaction is unlikely to form much product. In case of exothermic reactions, $\Delta_r H^\ominus$ is large and negative, and $\Delta_r G^\ominus$ is likely to be large and negative too. In such cases, K will be much larger than 1. We may expect strongly exothermic reactions to have a large K, and hence can go to near completion.

Using Eq. (4.14), we can determine the value of $\Delta_r G^\ominus$ if the value of K is known (or vice versa).

Example 4.7

Calculate $\Delta_r G^\ominus$ for conversion of oxygen to ozone $3/2\ O_2\ (g) \rightarrow O_3\ (g)$ at 298 K, if K_p for this conversion is 2.47×10^{-29}.

Solution

We know $\Delta_r G^\ominus = - 2.303\ RT \log K_p$ and $R = 8.314\ J/(K\ mol)$

Therefore, $\Delta_r G^\ominus = - 2.303\ (8.314\ J\ K^{-1}\ mol^{-1}) \times (298K)\ (\log 2.47 \times 10^{-29})$

$= 163000\ J\ mol^{-1}$

$= 163\ kJ\ mol^{-1}$.

Example 4.8

Find out the value of equilibrium constant for the following reaction at 298 K.

$2NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2(aq) + H_2O(l)$

Standard Gibbs energy change, $\Delta_r G^\ominus$ at the given temperature is $-13.6\ kJ\ mol^{-1}$.

Solution

We know, $$\log K = \frac{-\Delta_r G^\ominus}{2.303\ RT}$$

$$= \frac{(-13.6 \times 10^3\ J\ mol^{-1})}{2.303(8.314\ J\ K^{-1}\ mol^{-1})(298K)}$$

$= 2.38$

Hence K = antilog 2.38 = $10^{2.38} = 2.4 \times 10^2$.

SUMMARY

The first law of thermodynamics deals with conservation of energy but is silent about spontaneity of a chemical/physical change. Second law of thermodynamics explains why a physical/chemical change proceeds in one direction but not in the other. **Second law states that for a spontaneous process in an isolated system, the entropy change is positive**. Entropy is a measure of the chaotic dispersal of energy and matter, as dispersal increases so does the entropy. In brief, entropy is a measure of the degree of randomness or disorder in the system. For a spontaneous change, total entropy change (i.e., entropy change of the system + entropy change of the surroundings) is positive. This requires that

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0$

A system has a tendency to attain equilibrium. At equilibrium, entropy of an isolated system is maximum and entropy change is zero (i.e. at equilibrium $\Delta S = 0$). Entropy change during phase transformation can be calculated using equation $\Delta S = q_{rev}/T$. Entropy is function of temperature and it decreases if temperature decreases. Entropy of a solid substance is lower than its liquid and gaseous forms. **The entropy of a perfectly crystalline substance approaches zero as temperature approaches zero.** This is the **third law of thermodynamics.** Based on this law, standard molar entropy of a substance can be calculated at any specified temperature. Entropy change for a chemical reaction can be calculated using equation

$\Delta_r S_m^\ominus = \Sigma \nu_P S_m^\ominus$ (products) $- \Sigma \nu_R S_m^\ominus$ (reactants)

Gibbs energy is another thermodynamic function which is related to entropy (disorder) and enthalpy changes of the system by the equation

$\Delta_r G = \Delta_r H - T\Delta_r S$

For a spontaneous change, Gibbs energy change is negative i.e., $\Delta G_{system} < 0$ and at equilibrium, $\Delta G_{system} = 0$. Standard Gibbs energy of formation, $\Delta_f G^\ominus$ is the Gibbs energy change when one mole amount of a substance (compound) is formed in its standard state from its elements in their standard state at any specified temperature. Gibbs energy change of formation of a compound in its standard state can be calculated by

$\Delta_r G^\ominus = \Sigma \nu_P \Delta_f G^\ominus$ (products) $- \Sigma \nu_R \Delta_f G^\ominus$ (reactants)

Standard Gibbs energy change is related to equilibrium constant by

$\Delta_r G^\ominus = -RT \ln K$

When $\Delta_r G^\ominus$ is large and negative, the equilibrium lies strongly in favour of products; when it is large and positive, the equilibrium lies strongly in favour of reactants. The maximum quantity of non-expansion work per mole of reaction under standard conditions is equal to $\Delta_r G^\ominus$. Several reactions with positive Gibbs energy change can be made to take place on coupling with reactions having large negative Gibbs energy change. Such reactions are important in industry, metallurgy and in biosystems. Temperature is important factor in the equation, $\Delta G = \Delta H - T\Delta S$. Many reactions which are nonspontaneous at low temperatures, are made spontaneous by raising the temperature of the system having positive entropy of reaction.

EXERCISES

4.1 Define the following terms (to refresh your memory):

(a) System
(b) Isothermal and adiabatic processes
(c) State variables/state functions
(d) Work

4.2 State whether each of the following processes will increase or decrease total energy content of the system:
(a) Heat transferred to surroundings
(b) Work done by the system
(c) Work done on the system.

4.3 What do you mean by a spontaneous process? Explain your answer with suitable examples.

4.4 State second law of thermodynamics.

4.5 State third law of thermodynamics. Explain its implications.

4.6 Place the following systems in order of increasing randomness
(a) 1 mol of a gas X
(b) 1 mol of a solid X
(c) 1 mol of a liquid X.

4.7 Why would you expect a decrease in entropy as a gas condenses into liquid? Compare it with entropy decrease when a liquid sample is converted into solid.

4.8 Which of the following processes are accompanied by an increase of entropy:
(a) Dissolution of iodine in a solvent
(b) HCl is added to $AgNO_3$ solution and precipitate of AgCl is obtained
(c) A partition is removed to allow two gases to mix

4.9 Comment on the following statements:
(a) An exothermic reaction is always thermodynamically spontaneous
(b) The entropy of a substance increases on going from the liquid to the vapour state at any temperature
(c) Reaction with $\Delta_r G^\ominus < 0$ always have an equilibrium constant greater than 1

4.10 Predict the sign of the entropy change for each of the following changes of state
(a) $Hg\ (l) \rightarrow Hg\ (g)$
(b) $AgNO_3\ (s) \rightarrow AgNO_3\ (aq)$
(c) $I_2\ (g) \rightarrow I_2\ (s)$
(d) C (graphite) $\rightarrow$ C (diamond).

4.11 The enthalpy of vaporistaion of liquid diethyl ether – $(C_2H_5)_2O$, is 26.0 $kJmol^{-1}$ at its boiling point (35.0° C). Calculate $\Delta S^\ominus$ for conversion of:
(a) liquid to vapour, and
(b) vapour to liquid at 35.0° C.

4.12 Calculate the standard molar entropy change for formation of gaseous propane (C_3H_8) at 298 K.
$3C\ (graphite) + 4H_2\ (g) \rightarrow C_3H_8\ (g)$.

4.13 Calculate the standard molar entropy change for the following reactions at 298 K.
(a) $4Fe\ (s) + 3O_2\ (g) \rightarrow 2Fe_2O_3\ (s)$
(b) $Ca\ (s) + 2H_2O\ (l) \rightarrow Ca(OH)_2\ (aq) + H_2\ (g)$
(c) $Na_2CO_3\ (s) + 2HCl\ (aq) \rightarrow 2NaCl\ (aq) + H_2O\ (l) + CO_2\ (g)$.
(Necessary data can be obtained from the Appendix provided at the end).

4.14 Using the values of $\Delta_f H^\ominus$ and $\Delta_r S^\ominus$, calculate the standard molar Gibbs energy of formation, $\Delta_f G^\ominus$, for each of the following compounds:
(a) $CS_2\ (g)$
(b) $N_2H_4\ (l)$

4.15 Using the value of $\Delta_f G^\ominus$, calculate $\Delta_r G^\ominus$ for the following reactions. Which reactions are predicted to be spontaneous?
(a) $Ca\ (s) + Cl_2\ (g) \rightarrow CaCl_2\ (s)$
(b) $HgO\ (s) \rightarrow Hg\ (l) + ½\ O_2\ (g)$
(c) $NH_3\ (g) + 2O_2\ (g) \rightarrow HNO_3\ (l) + H_2O\ (l)$

4.16 In a fuel cell (a device for producing electricity directly from chemical reaction), methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

$$CH_3OH\ (l) + 3/2\ O_2\ (g) \rightarrow CO_2(g) + 2H_2O\ (l)$$

Calculate the standard Gibbs energy change for the reaction that can be converted into electrical work. If standard enthalpy of combustion for methanol is –726 $kJmol^{-1}$, calculate the efficiency* of conversion of Gibbs energy into useful work. (Please use the data of standard free energy of formation from the Table 4.3)

4.17 For the *water gas* reaction:

$$C\,(s) + H_2O\,(g) \rightleftharpoons CO\,(g) + H_2\,(g),$$

the standard Gibbs energy of reaction (at 1000K) is – 8.1 $kJmol^{-1}$. Calculate its equilibrium constant.

4.18 The standard Gibbs energies for the reactions at 1773 K are given below:

$C + O_2 \rightarrow CO_2$; $\Delta_r G^\ominus = -380\ kJmol^{-1}$

$2C + O_2 \rightleftharpoons 2CO$; $\Delta_r G^\ominus = -500\ kJmol^{-1}$

Discuss the possibility of reducing Al_2O_3 and PbO with carbon at this temperature.

$4Al + 3O_2 \rightarrow 2Al_2O_3$; $\Delta_r G^\ominus = -22500\ kJmol^{-1}$

$2Pb + O_2 \rightarrow 2PbO$; $\Delta_r G^\ominus = -120\ kJmol^{-1}$

4.19 Consider the following reaction:

$$2NO\,(g) + O_2\,(g) \rightarrow 2NO_2\,(g)$$

Calculate the value of standard Gibbs energy change at 298 K and predict whether the reaction is spontaneous or not.

4.20 It is planned to carry the reaction:

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

Calcite

at 1273 K at 1 bar.

(a) Is this reaction spontaneous at this temperature and pressure

(b) Calculate the value of

(i) K_p at 1273 K for the reaction and

(ii) partial pressure of CO_2 at equilibrium.

(Use tables provided in this Unit for necessary data)

4.21 How is the concept of coupling of reactions useful in explaining the occurrence of a nonspontaneous reaction?

4.22 Explain how the Gibbs energy changes as a spontaneous reaction occurs. Show with the help of a diagram how Gibbs energy changes with the extent of a reaction.

4.23 Calculate the standard Gibbs energy change, $\Delta_r G^\ominus$, of the following reactions at 298 K using standard Gibbs energy of formation:

(a) $CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g)$

(b) $CaCO_3\,(s) + 2H^+\,(aq) \rightarrow Ca^{2+}\,(aq) + H_2O\,(l) + CO_2\,(g)$

4.24 Sodium Carbonate, Na_2CO_3 can be obtained by heating sodium hydrogen carbonate, $NaHCO_3$

$$2NaHCO_3\,(s) \rightarrow Na_2CO_3\,(s) + H_2O\,(g) + CO_2\,(g)$$

Calculate the temperature above which $NaHCO_3$ decomposes to form products at 1bar. (Use the data given at the end of the book in the Appendix).

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* Efficiency = $\frac{\Delta G}{\Delta H}$

UNIT 5

ELECTROCHEMISTRY

OBJECTIVES

After studying this Unit, you will be able to:

- define resistivity (ρ), conductivity (κ) and molar conductivity (Λ) of ionic solutions.
- differentiate between ionic (electrolytic) and electronic conductivity.
- learn the method for measurement of conductivity of electrolytic solutions and calculation of their molar conductivity.
- justify the variation of conductivity and molar conductivity of solutions with change in their concentration and define, Λ^0 (molar conductivity at zero concentration or infinite dilution).
- enunciate Kohlraush law and learn its applications.
- describe an electrochemical cell and differentiate between galvanic and electrolytic cells.
- understand the quantitative aspects of electrolysis.
- use Nernst equation for calculating the emf of galvanic cell and define standard potential of the cell.
- develop relation between standard potential of the cell and Gibbs Energy of reaction and its equilibrium constant.
- describe the construction of some primary and secondary batteries and fuel cells.
- understand corrosion as an electrochemical process.

"Chemical affinity and electricity are one and the same."

- Michael Faraday

Electrochemistry is the study of the equilibrium and kinetic properties of ions in solution, production of electricity from energy released during spontaneous chemical reactions (Class XI, Unit 9) or its reverse when electrical energy is used to bring about non-spontaneous chemical transformations. The subject is of importance both for theoretical and practical considerations. A large number of metals, sodium hydroxide, chlorine, fluorine and many other chemicals are produced by electrochemical methods. Batteries and fuel cells convert chemical energy into electrical energy and are used on a large scale in various instruments and devices. Many fast and convenient analytical techniques are based on electrochemical principles. The transmission of sensory signals through cells to brain and vice versa and communication between the cells are known to have electrochemical origin. Electrochemistry, is therefore, a very vast and interdisciplinary subject. In this Unit, we will cover only some of its important elementary and basic aspects. First of all, let us consider how electricity is conducted through electrolytic solutions (i.e., solutions containing electrolytes) and how it differs from conduction through metals and alloys. We already know (Class XI, Unit 8) that electrolytes in their dissolved state in a polar solvent or in their molten state conduct electricity. The electrolytes produce ions on dissociation and conductance has been explained by movement of positive ions (called cations) and negative ions (called anions) under an electric field.

5.1 CONDUCTANCE OF ELECTROLYTIC SOLUTIONS

It is necessary to define a few terms before we consider the subject of conductance of electricity

through electrolytic solutions. The electrical resistance is represented by the symbol '*R*' and it is measured in ohm (Ω) which in terms of SI base units is equal to $(kg\ m^2)/(s^3\ A^2)$. It can be measured with the help of a Wheatstone bridge with which you are familiar from your study of physics. The electrical resistance of any object is directly proportional to its length, *l*, and inversely proportional to its area of cross section, *A*. That is,

$$R = l / A \text{ or } R = \rho\ (l/A) \qquad (5.1)$$

The constant of proportionality, ρ (Greek, rho), is called **resistivity** (specific resistance). Its SI units are ohm metre (Ω m) and quite often its submultiple, ohm centimetre (Ω cm) is also used. IUPAC recommends the use of the term resistivity over specific resistance and hence in the rest of the book we shall use the term resistivity. Physically, the resistivity for a substance is its resistance when it is one metre long and its area of cross section is one m^2. It can be seen that:

1 Ω m = 100 Ω cm or 1 Ω cm = 0.01 Ω m

The inverse of resistance, *R*, is called **conductance**, *G*, and we have the relation:

$$G = 1/R = A / (\rho\ l) = (A\ \kappa) / l \qquad (5.2)$$

The SI unit of conductance is siemens, represented by the symbol 'S' and is equal to ohm^{-1} (also known as mho) or Ω^{-1}. The inverse of resistivity, called conductivity (specific conductance) is represented by the symbol, κ (Greek, kappa). IUPAC has recommended the use of term conductivity over specific conductance and hence we shall use the term conductivity in the rest of the book. The SI units of conductivity are $S\ m^{-1}$ but quite often, κ is expressed in $S\ cm^{-1}$. Conductivity of a material in $S\ m^{-1}$ is its conductance when it is 1 m long and its area of cross section is 1 m^2. It may be noted that $1\ S\ cm^{-1} = 100\ S\ m^{-1}$.

It can be seen from Table 5.1 that the magnitude of conductivity varies a great deal and depends on the nature of the material. It also depends on the temperature and pressure at which the measurements are made. Materials are classified into conductors, insulators and semiconductors (Units 1 and 2) depending on the magnitude of their conductivity. Metals and their alloys have very large conductivity and are known as conductors. Substances like glass, ceramics etc. having very low conductivity are known as insulators. Substances like, silicon, doped silicon, gallium arsenide, having conductivity between conductors and insulators are called semiconductors and are important electronic materials. Certain materials called superconductors by definition have zero resistivity or infinite conductivity. Earlier only metals and their alloys at very low temperatures (0 to 15 K) were known to behave as superconductors, but nowadays a number of ceramic materials and mixed oxides are also known to show superconductivity at temperatures as high as 150 K.

We already know (Class XI, Unit 8) that even very pure water has small amounts of hydrogen and hydroxyl ions ($\sim 10^{-7}$ M) which lend it very low conductivity ($3.5 \times 10^{-5}\ S\ m^{-1}$). When electrolytes are dissolved in water, they furnish their own ions in the solution hence its conductivity also increases. The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance. The conductivity of electrolytic (ionic) solutions depends on:

- the nature of the electrolyte added
- size of the ions produced and their solvation
- the nature of the solvent and its viscosity
- concentration of the electrolyte
- temperature (it increases with the increase of temperature).

Passage of direct current through ionic solution over a prolonged period can lead to change in its composition due to electrochemical reactions (Section 5.1.1). Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on

- the nature and structure of the metal

Table 5.1 The values of Conductivity of some Selected Materials at 298.15 K

Material	Conductivity/ $S\ m^{-1}$	Material	Conductivity/ Sm^{-1}
Conductors		***Aqueous Solutions***	
Sodium	2.1×10^{3}	Pure water	3.5×10^{-5}
Copper	5.9×10^{3}	0.1 M HCl	3.91
Silver	6.2×10^{3}	0.01M KCl	0.14
Gold	4.5×10^{3}	0.01M NaCl	0.12
Iron	1.0×10^{3}	0.1 M HAc	0.047
Graphite	1.2×10	0.01M HAc	0.016
Insulators		***Semiconductors***	
Glass	1.0×10^{-16}	CuO	1×10^{-7}
Teflon	1.0×10^{-18}	Si	1.5×10^{-2}
		Ge	2.0

- the number of valence electrons per atom
- the density of metal
- temperature (it decreases with increase of temperature).

As the electrons enter at one end and go out at the other end, the composition of the metallic conductor remains unchanged. In contrast to electrolytic conductance, electronic conductance decreases with increase in temperature. The mechanism of conductance through semiconductors is more complex.

5.1.1 Measurement of the Conductivity of Ionic Solutions

We know that accurate measurement of an unknown resistance can be performed on a Wheatstone bridge. However, for measuring the resistance of an ionic solution we face two problems. Firstly, passing direct current (DC) changes the composition of the solution. Secondly, a solution of unknown resistance cannot be connected to the bridge like a metallic wire or other solid conductor. The first difficulty is resolved by using an alternating current (AC) source of power. The second problem is solved by using a specially designed vessel called **conductivity cell.** It is available in several designs and two simple ones are shown in (Fig. 5.1).

Basically it consists of two platinum electrodes coated with platinum black (finely divided metallic Pt is deposited on the electrodes electrochemically). These have area of cross section equal to 'A' and are separated by distance 'l'. Therefore, solution confined between these electrodes is a column of length l and area of cross section A. The resistance of such a column of solution is then given by the equation:

$$R = \rho\, l / A = l / \kappa A \qquad (5.3)$$

The quantity l/A is called cell constant denoted by the symbol, G^*. It depends on the distance between the electrodes and their area of cross-section and has the dimensions of length^{-1} and can be calculated if we know l and A. Experimental determination of l and A is not only inconvenient but also unreliable. The cell constant is usually determined by measuring the resistance of the cell containing a solution whose conductivity is already known. For this purpose, we generally use KCl solutions whose conductivity is known accurately at various concentrations (Table 5.2) and at different temperatures. The cell constant, G^*, is then given by the equation:

$$G^* = l/A = R\,\kappa \qquad (5.4)$$

Table 5.2 Conductivity and Molar Conductivity of KCl solutions at 298.15 K

Molarity	Concentration	Conductivity		Molar Conductivity	
mol L^{-1}	mol m^{-3}	S cm^{-1}	S m^{-1}	S cm^2 mol^{-1}	S m^2 mol^{-1}
1.000	1000	0.1113	11.13	111.3	111.3×10^{-4}
0.100	100.0	0.0129	1.29	129.0	129.0×10^{-4}
0.010	10.00	0.00141	0.141	141.0	141.0×10^{-4}

Once the cell constant is determined, we can use it for measuring the conductivity of any solution by filling the conductivity cell with it and measuring its resistance. The set up for the measurement of the resistance is shown in Fig. 5.2.

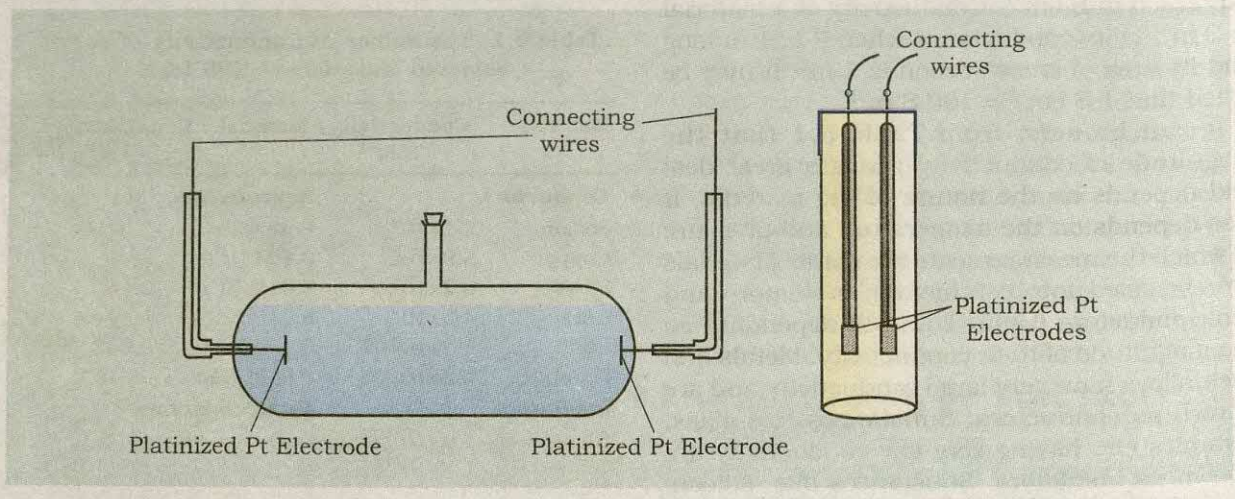


Fig. 5.1 *Two different types of conductivity cells.*

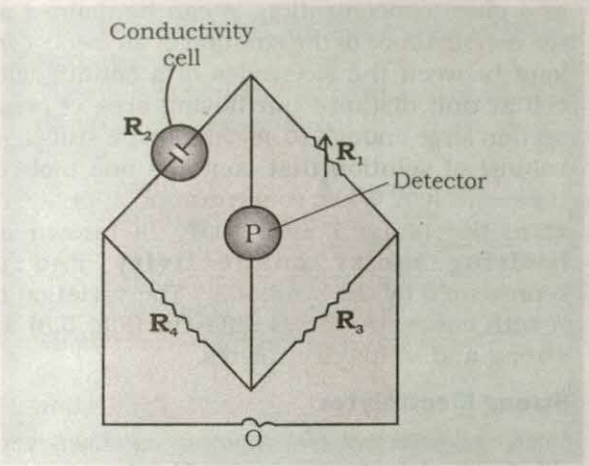


Fig. 5.2 *Arrangement for measurement of resistance of a solution of an electrolyte.*

It consists of two fixed resistances R_3 and R_4, a variable resistance R_1 and the conductivity cell having the unknown resistance R_2. The Wheatstone bridge is fed by an oscillator O (a source of a.c. power in the audio frequency range 550 to 5000 cycles per second). P is a suitable detector (a headphone or other electronic device) and the bridge is balanced when no current passes through the detector. Under these conditions:

Unknown resistance $R_2 = R_1 R_4 / R_3$

These days, inexpensive conductivity metres are available which can directly read the conductance or resistance of the solution in the conductivity cell. Once the cell constant and the resistance of the solution in the cell is determined, the conductivity of the solution is given by the equation:

κ = cell constant / R = G^* / R (5.5)

The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to charge and size of the ions in which they dissociate, the concentration of ions or ease with which the ions move under potential gradient. It, therefore, becomes necessary to define a physically more meaningful quantity called **molar conductivity** denoted by the symbol Λ (Greek, lambda). It is related to the conductivity of the solution by the equation:

Molar conductivity = $\Lambda = \kappa / c$ (5.6)

In the above equation, if κ is expressed in S m^{-1} and the concentration, c in mol m^{-3} then the units of Λ are in S m^2 mol^{-1}. It may be noted that:

1 mol m^{-3} = 1000(L/m^3) × molarity (mol/L), and hence

Λ(S m^2 mol^{-1}) = κ (S m^{-1})/[1000 L m^{-3} × molarity (mol L^{-1})]

If we use S cm^{-1} as the units for κ and mol cm^{-3}, the units of concentration, then the units for Λ are S cm^2 mol^{-1}. It can be calculated by using the equation:

$$\Lambda(\text{S cm}^2\text{ mol}^{-1}) = \frac{[\kappa\ (\text{S cm}^{-1}) \times 1000\ \text{cm}^3/\text{L}]}{\text{molarity (mol/L)}}$$

Both type of units are used in literature and are related to each other by the equations:

1 S m^2/mol = 10^4 S $cm^2 mol^{-1}$ or

1 S $cm^2 mol^{-1}$ = 10^{-4} S $m^2 mol^{-1}$.

Example 5.1

Resistance of a conductivity cell filled with 0.1M KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 M KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 M KCl solution. The conductivity of 0.1 M KCl solution is 1.29 S/m.

Solution

The cell constant is given by the equation:

Cell constant = G^* = conductivity × resistance

= 1.29 S/m × 100 Ω = 129 m^{-1} = 1.29 cm^{-1}

Conductivity of 0.02 M KCl solution = cell constant / resistance

= G^* / R = 129 m^{-1}/520 Ω = 0.248 S m^{-1}

Concentration = 0.02 mol / L

= 1000 × 0.02 mol / m^3

= 20 mol/m^3

Molar conductivity = $\Lambda = \kappa/c$

= 248 × 10^{-3} S m^{-1} / 20 mol m^{-3}

= 124 × 10^{-4} S $m^2 mol^{-1}$

Alternatively, κ = 1.29 cm^{-1}/ 520 Ω

= 0.248 × 10^{-2} S cm^{-1}

and $\Lambda = \kappa \times 1000\ cm^3\ L^{-1}$ / molarity

=(0.248×10^{-2} S cm^{-1}×1000 $cm^3 L^{-1}$)/0.02 mol L^{-1}

= 124 S cm^2 mol^{-1}

Example 5.2

The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55 × 10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Solution

$A = \pi r^2 = 3.14 \times 0.5^2\ cm^2 = 0.785\ cm^2$ or $0.785 \times 10^{-4}\ m^2$ and $l = 50$ cm or 0.5 m

$R = \rho\ l/A$ or

$\rho = R\ A/l = 5.55 \times 10^3 \Omega \times 0.785\ cm^2/\ 50\ cm$

$= 87.135\ \Omega$ cm

Conductivity = $\kappa = 1/\rho = (1/\ 87.135)\ S\ cm^{-1}$

$= 0.01148\ S\ cm^{-1}$

Molar conductivity, $\Lambda = \kappa \times 1000\ cm^3\ L^{-1}$/ molarity

$= 0.01148\ S\ cm^{-1} \times 1000\ cm^3 L^{-1}/0.05\ mol\ L^{-1}$

$= 229.\ 6\ S\ cm^2\ mol^{-1}$

If we want to calculate the values of different quantities in terms of 'm' instead of 'cm',

$\rho = R\ A\ /\ l$

$= 5.55 \times 10^3\ \Omega \times 0.785 \times 10^{-4}\ m^2/0.5\ m$

$= 87.135 \times 10^{-2}\ \Omega\ m$

$\kappa = 1/\rho = 100/87.135\ \Omega\ m = 1.148\ S\ m^{-1}$

and $\Lambda = \kappa\ /\ c = (1.148\ S\ m^{-1})/\ 50\ mol\ m^{-3}$

$= 229.6 \times 10^{-4}\ S\ m^2 mol^{-1}$.

5.1.2 Variation of Conductivity and Molar Conductivity with Concentration

Both conductivity and molar conductivity change with the concentration of the electrolyte. Conductivity always decreases with the decrease in concentration both for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution. The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length. This is clear from the equation:

$G = \kappa\ A/l = \kappa$ (both A and l are unity in their appropriate units in m or cm)

Molar conductivity increases with decrease in concentration. This is because the total volume, V, of solution containing one mole of electrolyte also increases and molar conductivity is the conductance of solution with unit length but the elecrtodes having area of cross section, $A = V$ with the result that $\Lambda = \kappa\ A/l$ but $l = 1$ and $A = V$ (volume containing 1 mole of electrolyte) and, therefore, $\Lambda = \kappa\ V$. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume. Physically, it means that at a given concentration, Λ can be defined as the conductance of the solution of an electrolyte kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. When concentration approaches zero, the molar conductivity is known as **limiting molar conductivity** and is represented by the symbol Λ^0. The variation in Λ with concentration is different (Fig. 5.3) for strong and weak electrolytes.

Strong Electrolytes

For strong electrolytes, Λ increases slowly with dilution and can be represented by the equation:

$$\Lambda = \Lambda^0 - A\ c^{1/2} \qquad (5.6)$$

It can be seen that if we plot (Fig. 5.3) Λ against $c^{1/2}$, we obtain a straight line with intercept equal to Λ^0 and slope equal to '-A'. The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. Thus, NaCl, $CaCl_2$, $MgSO_4$ are known as 1-1, 2-1 and 2-2 electrolytes respectively. All electrolytes of a particular type have the same value for 'A'.

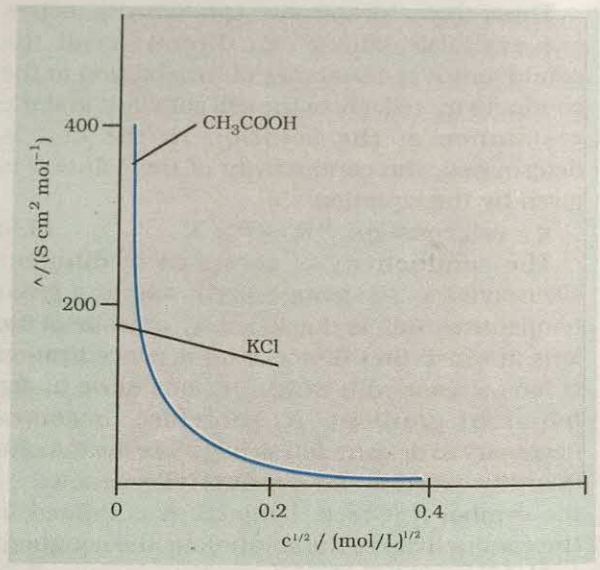


Fig. 5.3 *Molar conductivity versus c½ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte in aqueous solutions.*

Example 5.3

The molar conductivity of KCl solutions at different concentration at 298 K are given below:

c/mol L^{-1}	Λ/S cm^2 mol^{-1}
0.000198	148.61
0.000309	148.29
0.000521	147.81
0.000989	147.09

Show that a plot between Λ and $c^{1/2}$ is a straight line. Determine the values of Λ^0 and A for KCl.

Solution

Taking the square root of concentration we obtain:

$c^{1/2}$/ (mol L^{-1})$^{1/2}$	Λ / S $cm^2 mol^{-1}$
0.01407	148.61
0.01758	148.29
0.02283	147.81
0.03145	147.09

A plot of Λ(y-axis) and $c^{1/2}$ (x-axis) is shown in (Fig. 5.4). It can be seen that it is nearly a straight line. From the intercept ($c^{1/2}$ = 0), we find that Λ^0 = 149.8 S cm^2 mol^{-1} and

– slope = A = 87.46 S cm^2 mol^{-1}/(mol/L^{-1})$^{1/2}$.

Kohlrausch examined Λ^0 values for a number of strong electrolytes and observed certain regularities. He noted that the difference in Λ^0 of the electrolytes NaX and KX for any X is nearly constant. For example at 298 K:

$\Lambda^0_{KCl} - \Lambda^0_{NaCl} = \Lambda^0_{KBr} - \Lambda^0_{NaBr}$

$= \Lambda^0_{KI} - \Lambda^0_{NaI} \simeq 23.4$ S cm^2 mol^{-1}

and similarly it was found that

$\Lambda^0_{NaBr} - \Lambda^0_{NaCl} = \Lambda^0_{KBr} - \Lambda^0_{KCl} \simeq 1.8$ S cm^2 mol^{-1}

On the basis of the above observations he enunciated **Kohlrausch law of independent migration of ions**. The law states that *limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. Thus, if* $\lambda^\circ_{Na^+}$ *and* $\lambda^\circ_{Cl^-}$ *are limiting molar conductivity* of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:

$$\Lambda^0_{NaCl} = \lambda^0_{Na^+} + \lambda^0_{Cl^-} \quad (5.7)$$

In general, if an electrolyte on dissociation gives υ_+ cations and υ_- anions then its limiting molar conductivity is given by:

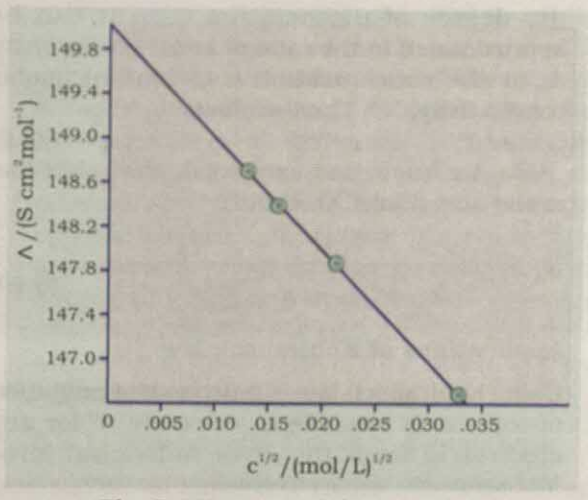


Fig. 5.4 *Variation of* Λ *against* $c^{1/2}$.

$$\Lambda^0 = \nu_+ \lambda^0_+ + \nu_- \lambda^0_- \quad (5.8)$$

Here, λ^0_+ and λ^0_- are the limiting molar conductivities of the cation and anion respectively. The values of λ^0 for some cations and anions at 298 K are given in Table 5.3.

Table 5.3 Limiting molar conductivity for some ions in water at 298 K

Ion	λ^0/(S cm^2mol^{-1})	Ion	λ^0/(S cm^2 mol^{-1})
H^+	349.6	OH^-	199.1
Na^+	50.1	Cl^-	76.3
K^+	73.5	Br^-	78.1
Ca^{2+}	119.0	CH_3COO^-	40.9
Mg^{2+}	106.0	SO_4^{2-}	160.0

Weak electrolytes

Weak electrolytes like acetic acid have lower degree of dissociation at higher concentration and hence for such electrolytes, the change in Λ with dilution is due to increase in the number of ions in total volume of solution that contains 1 mol of electrolyte. In such cases Λ increases steeply (Fig. 5.3) on dilution, especially near lower concentrations. Therefore, Λ^0 cannot be obtained by extrapolation of Λ to zero concentration. At infinite dilution (i.e., concentration c $\rightarrow$ zero) electrolyte dissociates completely (α =1), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately. Therefore, Λ^0 for weak electrolytes is obtained by using Kohlrausch law of independent migration of ions (Example 5.5). At any concentration c, if α is

the degree of dissociation then it can be approximated to the ratio of molar conductivity Λ_c at the concentration c to limiting molar conductivity, Λ^0. Thus we have:

$$\alpha = \Lambda/\Lambda^0 \qquad (5.9)$$

But we know that for a weak electrolyte like acetic acid (Class XI, Unit 8),

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda^2}{\Lambda^{\circ 2}\left(1-\Lambda/\Lambda^\circ\right)} = \frac{c\Lambda^2}{\Lambda^\circ\left(\Lambda^\circ-\Lambda\right)} \qquad (5.10)$$

Applications of Kohlrausch law

Using Kohlrausch law of independent migration of ions, it is possible to calculate Λ^0 for any electrolyte from the λ^0 of individual ions. Moreover, for weak electrolytes like acetic acid it is possible to determine the value of its dissociation constant once we know the Λ^0 and Λ at a given concentration c.

Example 5.4
Calculate Λ^0 for $CaCl_2$ and $MgSO_4$ from the data given in Table 5.3.

Solution:
We know from Kohlrausch law that

$\Lambda^0(CaCl_2) = \lambda^0(Ca^{2+}) + 2\lambda^0(Cl^-)$
$= 119.0\ S\ cm^2\ mol^{-1} + 2(76.3)\ S\ cm^2\ mol^{-1}$
$= (119.0 + 152.6)\ S\ cm^2\ mol^{-1}$
$= 271.6\ S\ cm^2\ mol^{-1}$
$\Lambda^0(MgSO_4) = \lambda^0(Mg^{2+}) + \lambda^0(SO_4^{2-})$
$= 106.0\ S\ cm^2\ mol^{-1} + 160.0\ S\ cm^2\ mol^{-1}$
$= 266\ S\ cm^2\ mol^{-1}$.

Example 5.5
Λ^0 for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. Calculate Λ^0 for HAc.

Solution

$\Lambda^0(HAc) = \lambda^0(H^+) + \lambda^0(Ac^-)$
$= \lambda^0(H^+) + \lambda^0(Cl^-) + \lambda^0(Ac^-) + \lambda^0(Na^+)$
$- \lambda^0(Cl^-) - \lambda^0(Na^+)$
$= \Lambda^0(HCl) + \Lambda^0(NaAc) - \Lambda^0(NaCl)$
$= (425.9 + 91.0 - 126.4)\ S\,cm^2\,mol^{-1}$
$= 390.5\ S\ cm^2\ mol^{-1}$.

Example 5.6
The conductivity of 0.001028 M acetic acid is 4.95×10^{-5} S cm^{-1}. Calculate its dissociation constant if Λ^0 for acetic acid is 390.5 S cm^2 mol^{-1}.

Solution

$$\Lambda = \frac{\kappa}{c} = \frac{4.95\times10^{-5}\,S\,cm^{-1}}{0.001028\,mol\,L^{-1}} \times \frac{1000\,cm^3}{L}$$
$$= 48.15\,S\,cm^2\,mol^{-1}$$
$$\alpha = \frac{\Lambda}{\Lambda^\circ} = \frac{48.15\,S\,cm^2\,mol^{-1}}{390.5\,S\,cm^2\,mol^{-1}} = 0.1233$$
$$K = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028\times(0.1233)^2}{1-0.1233} = 1.78\times10^{-5}$$

5.2 ELECTROCHEMICAL CELLS

In the previous section we noted that the conductance in an electrolytic solution is due to the movement of ions towards the oppositely charged electrodes under the applied electric field. If we apply a high frequency electric field, the direction of movement of ions reverses every time the polarity of the electrodes changes with the result that there is no net reaction at the electrodes. In this section, we shall study the reactions of ions at the electrodes in an electrochemical cell. In Class XI Unit 9 we had studied the construction and functioning of **Daniell cell** (Fig. 5.5). This cell converts the chemical energy liberated during the reaction

$$Zn(s) + Cu^{2+}(aq) = Zn^{2+}(aq) + Cu(s) \qquad (5.11)$$

to electrical energy and has an electrical potential equal to 1.1V when activity (nearly equal to molarity) of Zn^{2+} and Cu^{2+} ion is unity. Such a device is called a **galvanic** or a **voltaic** cell.

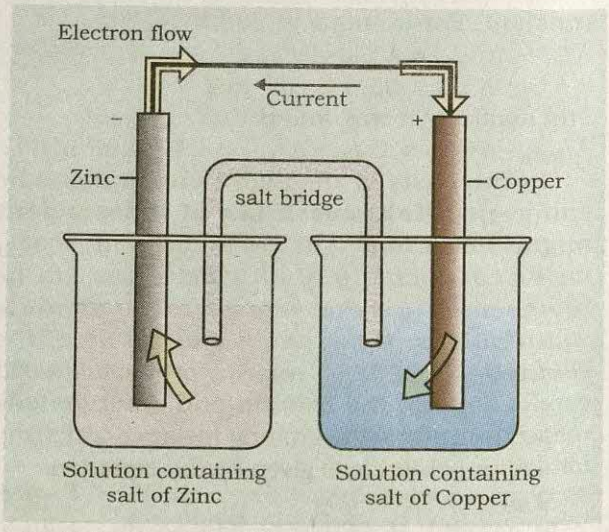
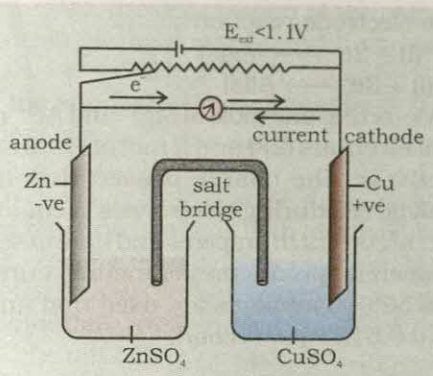
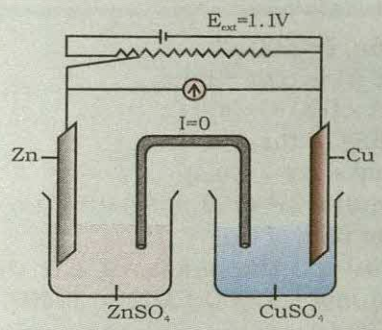


Fig. 5.5 *Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.*



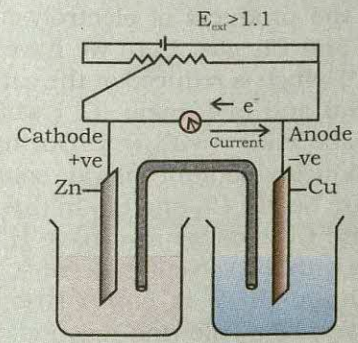
When E_{ext} < 1.1 V
(i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.
(ii) Zn dissolves at anode and copper deposits at cathode.

(a)



When E_{ext}=1.1V
(i) No flow of electrons or current .
(ii) No chemical reaction.

(b)



When E_{ext} >1.1V
(i) Electrons flow from Cu to Zn and current flows from Zn to Cu.
(ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

(c)

Fig. 5.6 *Functioning of Daniell cell when external voltage E_{ext} opposing the cell potential is applied.*

If an external opposite potential is applied [Fig. 5.6(a)] and increased slowly, we find that the reaction continues to take place till the opposing voltage reaches the value 1.1 V [Fig. 5.6(b)] when the reaction stops altogether and no current flows through the cell. Further increase in the external potential now again starts the reaction but in the opposite direction [Fig. 5.6(c)]. It now functions as an electrolytic cell; a device for using electrical energy to carry non-spontaneous chemical reactions. Both types of cells are quite important and we shall study some of their salient features in the following pages.

5.2.1 Electrolytic Cells and Electrolysis

In an **electrolytic cell** external source of voltage is used to bring about a chemical reaction. The electrochemical processes are of great importance in the laboratory and the chemical industry. One of the simplest electrolytic cell consists of two copper strips dipping in an aqueous solution of copper sulphate. Now if a DC voltage is applied to the two electrodes, then Cu^{2+} ions discharge at the cathode (negatively charged) and the following reaction takes place:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu\ (s) \qquad (5.12)$$

Copper metal is deposited on the cathode. At the anode copper is converted into Cu^{2+} ions by the reaction:

$$Cu(s) \rightarrow Cu^{2+}(s) + 2e^- \qquad (5.13)$$

Thus copper is dissolved (oxidised) at anode and deposited (reduced) at cathode. This is the basis for an industrial process in which impure copper is converted into copper of high purity. The impure copper is made an anode that dissolves on passing current and pure copper is deposited at cathode. Many metals like Na, Mg, Al, etc. are produced on large scale by electrochemical reduction of their respective cations whereas no suitable chemical reducing agents are available for this purpose.

Sodium and magnesium metals (Class XI, Unit 12) are produced by the electrolysis of their fused chlorides and aluminium is produced (Unit 8) by electrolysis of aluminium oxide in presence of cryolite.

Quantitative aspects of electrolysis

Faraday was the first scientist who described the quantitative aspects of electrolysis.

Faraday's Laws of Electrolysis

After his extensive investigations on electrolysis of solutions and melts of electrolytes, Faraday published his results during 1833-34 in the form of following well known Faraday's two laws of electrolysis:

1. **First Law**: The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).
2. **Second Law**: The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution is proportional to their chemical equivalent weights (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation).

There were no constant current sources available during Faraday's times. The general practice was to put a coulometer (a standard electrolytic cell) for determining the quantity of electricity from the amount of metal (generally silver or copper) deposited or consumed. However, coulometers are now obsolete and we have now constant current (I) sources available and the quantity of electricity Q, passed is given by

$$Q = It$$

Q is in coloumbs when I is in ampere and t is in second.

His two laws of electrolysis in their modern combined version may be stated as: the amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction. For example, in the reaction:

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad (5.14)$$

One mole of the electron is required for the reduction of one mole of silver ions. We know that charge on one electron is equal to 1.6021×10^{-19}C. Therefore charge on one mole of electrons is equal to:

$$N_A \times 1.6021 \times 10^{-19}\text{C} = 6.02 \times 10^{23}\text{mol}^{-1} \times 1.6021 \times 10^{-19}\text{C} = 96487\ \text{C mol}^{-1}$$

This quantity of electricity is called **Faraday constant** and is represented by the symbol ***F***. For approximate calculations we use $1F \simeq 96500\ \text{C mol}^{-1}$.

For the electrode reactions:

$$Mg^{2+}(l) + 2e^- \longrightarrow Mg(s) \qquad (5.15)$$

$$Al^{3+}(l) + 3e^- \longrightarrow Al(s) \qquad (5.16)$$

it is obvious that one mole of Mg^{2+} and Al^{3+} require 2 mol of electrons (2F) and 3 mol of electrons (3F) respectively. The charge passed through the electrolytic cell during electrolysis is equal to the product of current in amperes and time in seconds. In commercial production of metals, current as high as 50,000 amperes are used that amounts to about 0.518 F per second.

Example 5.7

A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?

Solution: $t = 600$ s

charge = current × time

$= 1.5\ \text{A} \times 600\ \text{s} = 900\ \text{C}$

According to the reaction:

$Cu^{2+}(aq) + 2e^- = Cu(s)$

We require 2F or 2×96487 C to deposit 1 mol or 63 g of Cu.

For 900 C, the mass of Cu deposited $= (63\ \text{g mol}^{-1} \times 900\ \text{C})/(2 \times 96487\ \text{C mol}^{-1}) = 0.2938$ g .

Products of electrolysis depend on the state of material being electrolysed and the type of electrodes being used. For example, if we use molten NaCl, the products of electrolysis are sodium metal and Cl_2 gas. Here we have only one cation (Na^+) which is reduced at the cathode ($Na^+ + e^- \rightarrow Na$) and one anion ($Cl^-$) which is oxidized at the anode ($Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$). During the electrolysis of aqueous sodium chloride solution, the products are NaOH, Cl_2 and H_2. In this case besides Na^+ and Cl^- ions we also have H^+ and OH^- ions along with the solvent molecules, H_2O.

At the cathode there is competition for reduction between the following reactions:

$Na^+(aq) + e^- \rightarrow Na(s)$ $\qquad E^\ominus = -2.71$ V

$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$ $\qquad E^\ominus = 0.00$ V

The reaction with higher value of $E^\ominus$ is preferred and, therefore, the reaction at the cathode during electrolysis is:

$$H^+(aq) + e^- \rightarrow \tfrac{1}{2}H_2(g) \qquad (I)$$

but $H^+(aq)$ is produced by the dissociation of H_2O, i.e.,

$$H_2O(l) \rightarrow H^+(aq) + OH^-(aq) \qquad (II)$$

Therefore, the net reaction at the cathode may be written as the sum of I and II and we have

$H_2O\ (l) + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-$ (III)

At the anode the following oxidation reactions are possible:

$Cl^-(aq) \rightarrow \frac{1}{2}\ Cl_2\ (g) + e^-$ $\quad :E^\ominus = 1.36$ V (IV)

$2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+(aq) + 4e^-$ $\quad :E^\ominus = +1.23$ V

The reaction at anode with lower value of $E^\ominus$ is preferred and therefore, water should get oxidised in preference to Cl^- (aq). However, on account of overpotential of oxygen, reaction (IV) is preferred. Thus, the net reactions may be summarized as:

$NaCl\ (aq) \xrightarrow{H_2O} Na^+\ (aq) + Cl^-\ (aq)$

Cathode $\quad H_2O(l) + e^- \rightarrow \frac{1}{2}\ H_2(g) + OH^-\ (aq)$

Anode $\quad Cl^-\ (aq) \rightarrow \frac{1}{2}\ Cl_2(g) + e^-$

Net reaction:

$NaCl(aq) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$

The standard electrode potentials are replaced by electrode potentials given by Nernst equation (Eq. 5.22) to take into account the concentration effects. During the electrolysis of sulphuric acid following processes are possible at the anode:

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-;\ E^\ominus = +1.23$ V, (V)

$2SO_4^{2-}\ (aq) \rightarrow S_2O_8^{2-}\ (aq) + 2e^-;\ E^\ominus = 1.96$ V (VI)

For dilute sulphuric acid, reaction (V) is preferred but at higher concentration of H_2SO_4 process, (VI) is preferred. If the electrode is inert (e.g., platinum or gold), it does not participate in the chemical reaction and acts only as source or sink for electrons. On the other hand if the electrode is reactive, it participates in the electrode reaction. Thus, the products of electrolysis may be different for reactive and inert electrodes.The products of electrolysis depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials. Moreover, some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these don't seem to take place and extra potential (called *overpotential*) has to be applied.

5.2.2 Galvanic Cells

As mentioned earlier (Class XI, Unit 9) a galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous reaction into electrical energy. We can use the device for converting Gibbs energy of the spontaneous chemical reaction into electrical work (for example, driving a motor or passing a current through a heater, etc.). We can construct innumerable number of galvanic cells on the pattern of Daniell cell in which the redox reaction:

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ (5.11)

can be split into two reduction half reactions.

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ (5.17)

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ (5.18)

The difference between the two half reactions [(5.17) – (5.18)] gives the overall cell reaction (5.11). All galvanic cells consist of two half cells. Each half cell consists of a metallic electrode dipping into an electrolyte. The half cell in which oxidation take place is called anode and it has negative potential with respect to solution. The other half cell in which reduction takes place is called cathode and has positive potential with respect to solution. The two half cells are connected by a metallic wire through a voltmeter and a switch externally and the electrolytes of two half cells are connected through a salt bridge as shown in the (Fig. 5.5).

Sometimes both the electrodes dip in the same electrolyte solution and in such cases we don't require salt bridge. A galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge. Conventionally, for a spontaneous reaction taking place towards right hand side, the potential difference between the two electrodes should be positive and for this purpose the **cathode is written on the right hand side and the anode is written on the left hand side.** This is illustrated by some examples given below.

Cell reaction:

$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\ Ag(s)$ (5.19)

Half cell reactions:

$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$ (5.20)

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ (5.21)

It can be seen that [(5.20)-(5.21)] leads to overall reaction (5.19) in the cell and that silver electrode acts as a cathode and copper electrode acts as an anode. The cell can be represented by:

$$Cu(s)\,|\,Cu^{2+}(aq)\,||\,Ag^+(aq)\,|\,Ag\ (s)$$

and we have $E_{cell} = E_{right} - E_{left} = E_{Ag^+|Ag} - E_{Cu^{2+}|Cu}$

Sometimes metals like platinum or gold are used as inert electrodes. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for the conduction of electrons. For example, Pt is used

in following half cells:
Hydrogen electrode: $Pt,H_2(g) \mid H^+(aq)$
with half cell reaction: $H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g)$
Bromine electrode: $Pt,Br_2(aq) \mid Br^-(aq)$ with half cell reaction: $\frac{1}{2} Br_2(aq) + e^- \rightarrow Br^-(aq)$

Sometimes metals in contact with their solid salts are also used as electrodes. For example, we have:

Silver-Silver chloride electrode:
$Ag, AgCl(s) \mid Cl^-(aq)$,
half cell reaction : $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$

Mercury-Mercurous chloride electrode:
$Hg(l), Hg_2Cl_2(s) \mid Cl^-(aq)$,
half cell reaction: $\frac{1}{2}Hg_2Cl_2(s) + e^- \rightarrow Hg(l) + Cl^-(aq)$

The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts. The cell potential is the difference between the electrical potentials at the cathode and anode. It is also called the emf of the cell when the cell is used in such a manner that no current is drawn through the cell. It is not possible to measure the absolute potential of an electrode individually as for electrical connection we always need a second electrode. We can arbitrarily define the potential of any electrode as zero and then assign the electrical potential of other electrodes relative to this reference electrode. For this purpose, a *Standard Hydrogen Electrode* (SHE) has been selected to have zero standard potential at all temperatures. It consists of a platinum foil coated with platinum black (finely divided platinum) dipping partially into an aqueous solution in which the activity (approximate concentration 1M) of hydrogen ion is unity and hydrogen gas is bubbled through the solution at 1 bar pressure (Fig. 5.7).

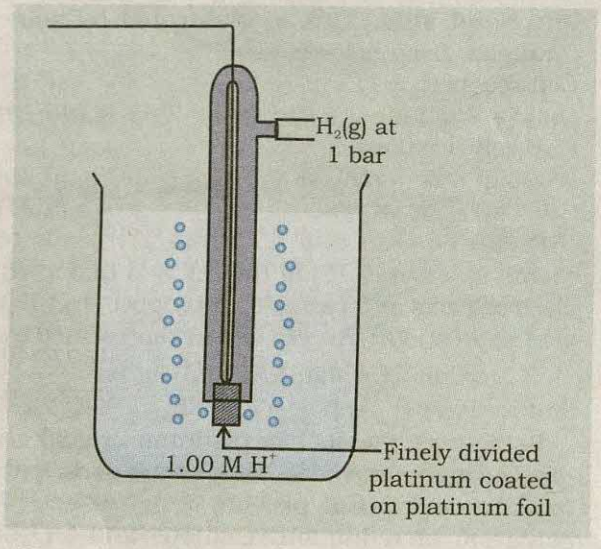


Fig. 5.7 *Standard Hydrogen Electrode (SHE).*

The potential of the other half cell is measured by constructing a cell in which reference electrode is standard hydrogen electrode. The potential of the other half cell is equal to the potential of the cell. If the activity of all the participating species at the other electrode is unity, then the measured potential is called standard potential ($E^\ominus$) of the electrode. The activities of solids and liquids are taken as unity and at low concentrations, the activity of a solute is approximated to its molarity. For example, we have the cells:

$Pt(s) \mid H_2(g), 1bar \mid H^+(aq) 1M \,||\, Ag^+(aq)\ 1M \mid Ag(s)$
$E^o(Ag^+, Ag) = 0.80\ V$
$Pt(s) \mid H_2(g), 1bar \mid H^+(aq) 1M \,||\, Zn^{2+}(aq) 1M \mid Zn(s)$
$E^o(Zn^{2+}, Zn) = -0.76\ V$

The values of standard potentials at 298 K are given in Table 5.4 for some selected half cells.

The overall standard potential of a cell formed by any two electrodes can be calculated by taking the difference in their standard potential i.e., by subtracting the standard potential of the anode from the standard potential of the cathode i.e.,

$$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$$

The greater value of E^o for a half cell indicates that the reductant in the half cell is stronger reducing agent than the H_2 gas. The arrangement of metals in their increasing reducing power (or decreasing $E^\ominus$) is known as **electrochemical series.**

5.2.3 Nernst Equation

We have noted in the previous section that the activity of all the species involved in the electrode reaction is unity. This need not be always true. Nernst showed that for the electrode reaction:
$M^{n+}(aq) + ne^- \rightarrow M(s)$,
the potential of the electrode at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E(M^{n+},M) = E^\ominus(M^{n+},M) - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

but activity of solid M is unity and we have

$$E(M^{n+},M) = E^\ominus(M^{n+},M) + \frac{RT}{nF} \ln[M^{n+}] \qquad (5.22)$$

$E^\ominus(M^{n+}, M)$ has already been defined, R is gas constant ($8.314\ JK^{-1}mol^{-1}$) and F is Faraday

Table 5.4 The standard electrode potentials at 298 K

Ions are present as aqueous species and H_2O as liquid; gases and solids are shown by g and s.

Reaction (Oxidized form + ne^-	→ Reduced form)	$E^\ominus$/V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2 + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	**$\rightarrow H_2(g)$**	**0.00**
$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	−0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	−0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$	−0.25
$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	−0.44
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	−0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	−0.76
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+} + 3e^-$	$\rightarrow Al(s)$	−1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$	−2.36
$Na^+ + e^-$	$\rightarrow Na(s)$	−2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	−2.87
$K^+ + e^-$	$\rightarrow K(s)$	−2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	−3.05

Increasing strength of oxidising agent ↑

Increasing strength of reducing agent ↓

1. A negative $E^\ominus$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
2. A positive $E^\ominus$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

constant, T is temperature in kelvin. and $[M^{n+}]$ is the concentration of the species, M^{n+}.

In Daniell cell the electrode potential for any given concentration of Cu^{2+} and Zn^{2+} ions, we write For Cathode:

$$E(Cu^{2+},Cu) = E^{\ominus}(Cu^{2+},Cu) + \frac{RT}{2F}\ln[Cu^{2+}(aq)] \quad (5.23)$$

For Anode:

$$E(Zn^{2+},Zn) = E^{\ominus}(Zn^{2+},Zn) + \frac{RT}{2F}\ln[Zn^{2+}(aq)] \quad (5.24)$$

The cell potential, $E = E(Cu^{2+}, Cu) - E(Zn^{2+},Zn)$

$$= E^{\ominus}(Cu^{2+}, Cu) + \frac{RT}{2F}\ln[Cu^{2+}(aq)] - E^{\ominus}(Zn^{2+}, Zn) - \frac{RT}{2F}\ln[Zn^{2+}(aq)]$$

$$= E^{\ominus}(Cu^{2+}, Cu) - E^{\ominus}(Zn^{2+}, Zn) + \frac{RT}{2F}[\ln(Cu^{2+}) - \ln(Zn^{2+})]$$

$$E = E^{\ominus}(cell) + \frac{RT}{2F}\ln\frac{[Cu^{2+}]}{[Zn^{2+}]} \quad (5.25)$$

It can be seen that E depends on the concentration of both Cu^{2+} and Zn^{2+} ions. It increases with increase in the concentration of Cu^{2+} ions and with the decrease in the concentration of Zn^{2+} ions.

By converting the natural logarithm in Eq. (5.25) to the base 10 and substituting the values of R, F and T = 298 K, it reduces to

$$E = E^{\ominus}(cell) + \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Zn^{2+}]} \quad (5.25a)$$

We should use the same number of electrons (n) for both the electrodes and thus for the cell $Ni(s)\,|Ni^{2+}(aq)\,||\,Ag^{+}(aq)\,|Ag$. The cell reaction is $Ni(s) + 2Ag^{+}(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$.

The Nernst equation can be written as

$$E = E^{\ominus}(cell) + \frac{RT}{2F}\ln\frac{[Ag^{+}]^2}{[Ni^{2+}]}$$

and for a general electrochemical reaction of the type:

$$aA + bB \xrightarrow{ne^-} cC + dD$$

the Nernst equation can be written as:

$$E = E^{\ominus}(cell) - \frac{RT}{nF}\ln Q$$

$$= E^{\ominus}(cell) - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$\text{or } E = E^{\ominus}(cell) + \frac{RT}{nF}\ln\frac{[A]^a[B]^b}{[C]^c[D]^d} \quad (5.26)$$

Example 5.8

Represent the cell in which the following reaction takes place

$Mg(s) + 2Ag^{+}(0.0001M) \rightarrow Mg^{2+}(0.130M) + 2Ag(s)$

Calculate its E if $E^{\ominus} = 3.17$ V.

Solution

The cell can be written as

$Mg\,|Mg^{2+}(0.130M)\,||\,Ag^{+}(0.0001M)\,|Ag.$

$$E = E^{\ominus}(cell) + \frac{RT}{2F}\ln\frac{[Ag^{+}]^2}{[Mg^{2+}]}$$

$$= 3.17\text{ V} + \frac{0.059V}{2}\log\frac{(0.0001)^2}{0.130} = 3.17\text{ V} - 0.21\text{V}$$

$$= 2.96\text{ V}.$$

A cell in which both electrodes are of the same type but the solutions of electrolyte in which they dip have different concentrations is called **concentration cell.** For example, in the concentration cell [Fig. (5.8)]:

$Cu\,|CuSO_4(c_1)\,||\,CuSO_4(c_2)\,|Cu$, the standard potential of the two electrodes will cancel and the cell potential is given by the equation:

$E(cell) = (RT/2F)\ln(c_2/c_1)$

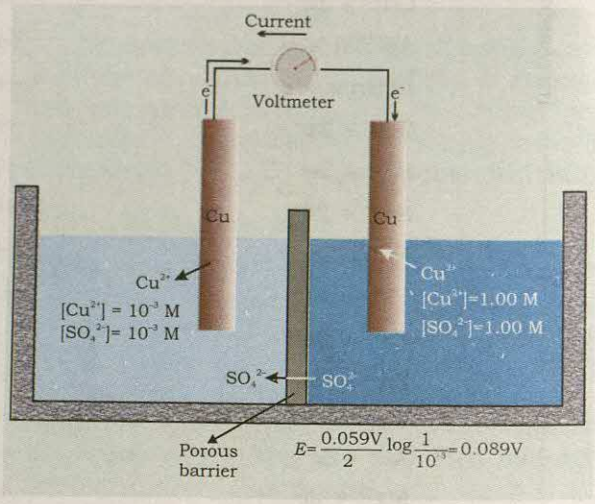


Fig. 5.8 *A copper ion concentration cell.*

5.2.4 Equilibrium Constant from Nernst Equation

If the Daniell cell (Fig. 5.5) is short circuited then we note that the reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad (5.11)$$

takes place and as the time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu^{2+} keeps on decreasing. At the same time voltage of the cell as read on the voltmeter keeps on decreasing. After some time, we shall note that there is no change in the concentration of Cu^{2+} and Zn^{2+} ions and at the same time, voltmeter gives zero reading. This indicates that the equilibrium has been attained. In this situation the Nernst equation may be written as:

$$E = 0 = E^{\ominus}(\text{cell}) + \frac{2.303RT}{2F} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$\text{or } E^{\ominus}(\text{cell}) = -\frac{2.303RT}{2F} \log \frac{[Cu^{2+}]}{[Zn^{2+}]} = \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium,

$\frac{[Zn^{2+}]}{[Cu^{2+}]} = K_c$ for the reaction (5.11)

and the above equation can be written as

$$E^{\ominus}(\text{cell}) = \frac{0.059V}{2} \log K_C = 1.1 \text{ V } (E^{\ominus} = 1.1V)$$

$\log K_C = (1.1V \times 2)/ 0.059 V$

$K_C = 2 \times 10^{37}$ at 298K. In general,

$$E^{\ominus}(\text{cell}) = \frac{2.303RT}{nF} \log K_C \qquad (5.27)$$

Thus, Eq. (5.27) gives a relationship between equilibrium constant of the reaction and standard potential of the cell in which that reaction takes place. Thus, equilibrium constants of the reactions difficult to measure otherwise, can be calculated from the corresponding $E^{\ominus}$ value of the cell.

Example 5.9
Calculate the equilibrium constant of the reaction:
$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$
$E^{\ominus} = 0.46$ V

Solution

$$E^{\ominus}(\text{cell}) = \frac{0.059V}{2} \log K_C \text{ or}$$

$$\log K_C = \frac{0.46V \times 2}{0.059\,V} = 15.6$$

$K_C = 3.92 \times 10^{15}$.

5.2.5 Electrochemical Cell and Gibbs Energy of the Reaction

Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf (it is the potential of the cell when no current is drawn) of the cell is E and nF is the amount of charge passed and $\Delta_r G$ is the Gibbs energy of the reaction then

$\Delta_r G = - nF E$ (5.28)

It may be remembered that E is an intensive parameter but $\Delta_r G$ is an extensive thermodynamic property and the value depends on n. Thus, if we write the reaction

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$ (5.11)

$\Delta_r G = -2FE$

but when we write the reaction

$2\,Zn\,(s) + 2\,Cu^{2+}(aq) \longrightarrow 2\,Zn^{2+}(aq) + 2\,Cu(s)$ (5.11a)

$\Delta_r G = -4FE$

If the activity of all the reacting species is unity, then $E = E^{\ominus}$ and we have

$\Delta_r G^{\ominus} = -nFE^{\ominus}$ (5.29)

Thus, from the measurement of $E^{\ominus}$ we can obtain an important thermodynamic quantity. From the temperature dependence of $E^{\ominus}$ we can also calculate $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$. From the standard Gibbs energy we can calculate equilibrium constant by the equation:

$\Delta_r G^{\ominus} = -RT \ln K$.

Example 5.10
The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction:
$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

Solution

$\Delta_r G^{\ominus} = - nFE^{\ominus}$

n in the above equation is 2 and F = 96487 C

Therefore, $\Delta_r G^{\ominus} = -2 \times 1.1V \times 96487\ C\ mol^{-1}$

$= -21227\ J\ mol^{-1}$

$= -21.227\ kJ\ mol^{-1}$.

5.3 BATTERIES

Any battery (actually it may have one or more than one cell connected in series) or cell that we use as a source of electrical energy is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy.

However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. There are mainly two types of batteries.

Primary Batteries

In the primary batteries, the reaction occurs only once and battery then becomes dead after use over a period of time and cannot be reused again. The most familiar example of this type is the dry cell (known as Leclanche cell after its discoverer) which is used commonly in our transistors and clocks. The cell consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon (Fig.5.9). The space between the electrodes is filled by a moist paste of NH_4Cl and $ZnCl_2$. The electrode reactions are complex, but they can be written approximately as follows :

Anode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

Cathode: $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

In the reaction at cathode, manganese is reduced from the +4 oxidation state to the +3 state. Ammonia produced in the reaction forms complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V.

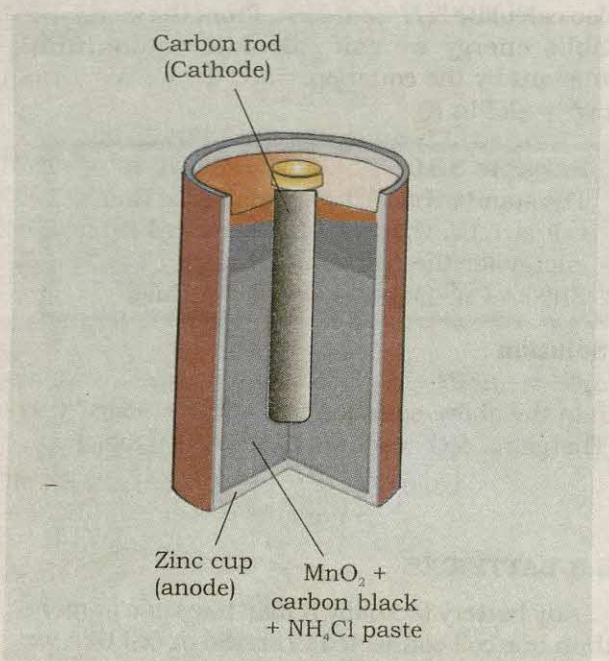


Fig. 5.9 *A commercial dry cell consists of a graphite (carbon) cathode in a zinc container; the latter acts as the anode.*

Mercury cell (Fig. 5.10) suitable for the low current devices like hearing aids and camera, etc. consists of zinc – mercury amalgam as anode and a paste of HgO and carbon as the cathode . The electrolyte is a paste of KOH and ZnO. The electrode reactions for the cell are given below:

Anode: $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

Cathode: $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

The overall reaction is represented by

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

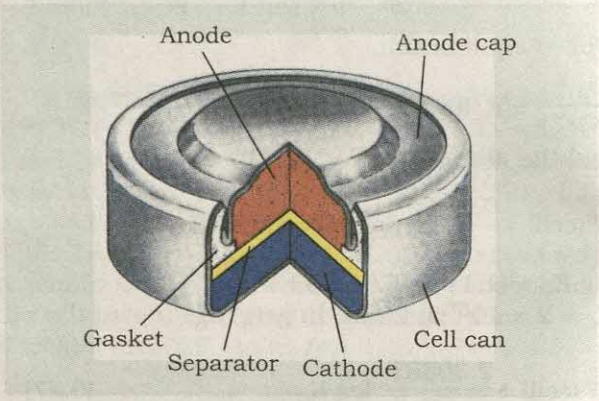


Fig. 5.10 *Commonly used mercury cell. The reducing agent is zinc and the oxidising agent is mercury (II) oxide.*

Secondary Batteries

A secondary cell after use can be recharged by passing current through it in opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles. The most important secondary cell is the lead storage battery (Fig. 5.11) commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

The cell reactions when the battery is in use are given below:

Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

i.e., overall cell reaction consisting of cathode and anode reactions is:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2, respectively.

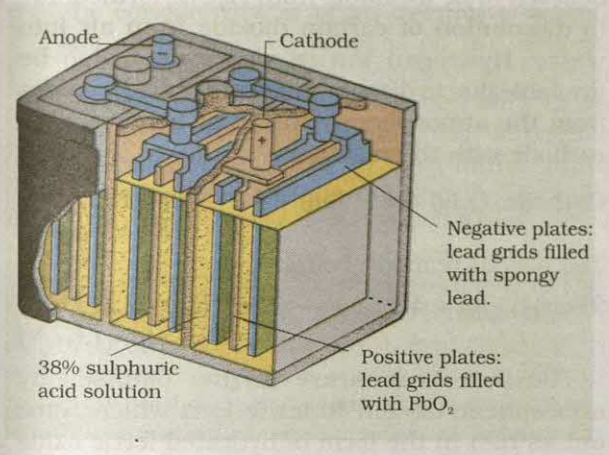


Fig. 5.11 *The Lead storage battery.*

Another important secondary cell is the nickel-cadmium cell (Fig. 5.12) which has longer life than the lead storage cell but more expensive to manufacture. We shall not go into details of working of the cell and the electrode reactions during charging and discharging. The overall reaction during discharge is:

$$Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$$

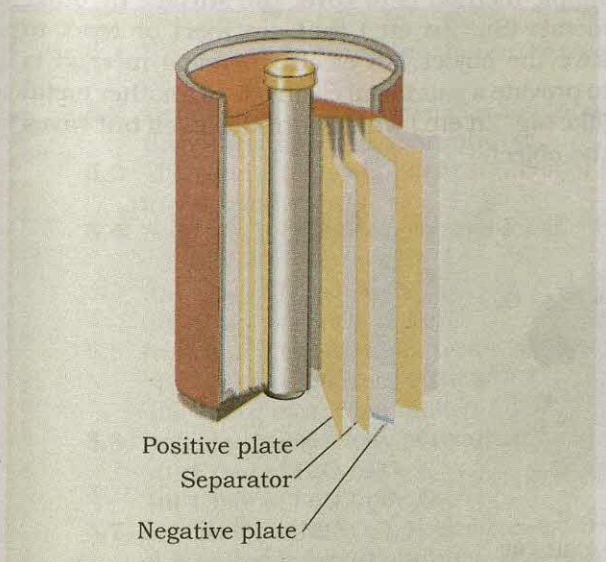


Fig. 5.12 *A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.*

5.4 FUEL CELLS

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run a turbine to produce electricity. We know that a galvanic cell directly converts chemical energy into electricity and is highly efficient. It is now possible to make such cells in which reactants are fed continuously to the electrodes and products are removed continously from the electrolyte compartment. Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol etc. directly into electrical energy are called **fuel cells**.

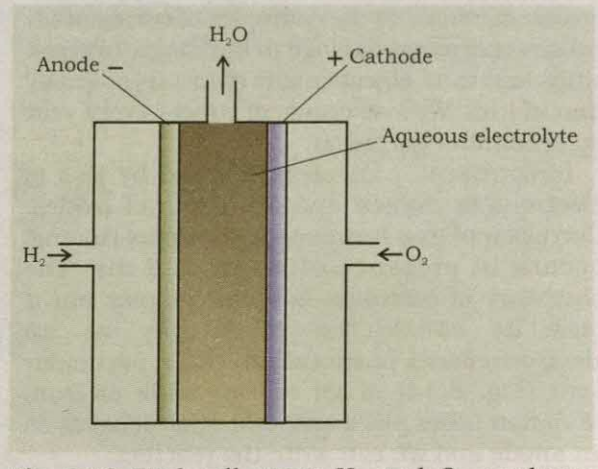


Fig. 5.13 *Fuel cell using H_2 and O_2 produces electricity.*

One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water (Fig. 5.13). The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Anode: $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

Overall reaction being:

$2H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$

The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70 % compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells. These have been used in automobiles on experimental basis. Fuel cells are pollution free and in view of their importance in future a variety of fuel cells have been fabricated and tried.

5.5 CORROSION

Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion. It causes enormous damage to buildings, bridges, ships and to all objects made of metals specially that of iron. We lose crores of rupees every year on account of corrosion.

In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon. At a particular spot (Fig. 5.14) of an object made of iron, oxidation takes place and that spot behaves as an anode and we can write the reaction:

Anode: $2\ Fe\ (s) \longrightarrow 2\ Fe^{2+} + 4\ e^-$

$E^\ominus\ (Fe^{2+}, Fe) = -0.44\ V$

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as a cathode with the reaction:

Cathode: $O_2(g) + 4\ H^+(aq) + 4\ e^- \longrightarrow 2\ H_2O\ (l)$

$(E^\ominus = 1.23\ V)$

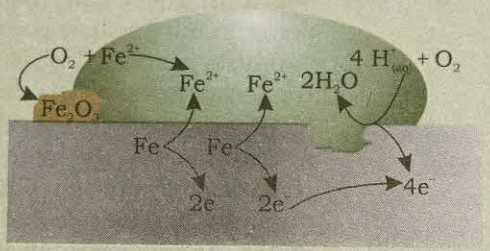
The overall reaction being:

$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2\ H_2O\ (l)$

$[E^\ominus\ (cell) = 1.67\ V]$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($Fe_2O_3 . x\ H_2O$) and with further production of hydrogen ions.

Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion. One of the simplest method of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by covering the surface by paint or by some chemicals (e.g. bisphenol). Other simple method is to cover the surface by other metals (Sn, Zn etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn etc.) which corrodes itself but saves the object.



Oxidation: $Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e$

Reduction: $O_2\ (g) + 4H^+(aq) + 4e \rightarrow 2H_2O(l)$

Atomospheric oxidation : $2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \rightarrow Fe_2O_3(s) + 4H^+(aq)$

Fig. 5.14 *Corrosion of iron in atmosphere.*

SUMMARY

The conductivity, κ, of an electrolytic solution is defined in the same way as that for any other object. It depends on the concentration of the electrolyte, nature of solvent and temperature. Molar conductivity, Λ, is defined by $\Lambda = \kappa/c$. Conductivity decreases but molar conductivity increases with decrease in concentration. Λ increases slowly with decrease in concentration for strong electrolytes while the increase is very steep for weak electrolytes in very dilute solutions. Kohlrausch found that Λ^0 molar conductivity at infinite dilution, for an electrolyte is sum of the contribution of the molar conductivity of the ions in which it dissociates. It is known as *law of independent migration of ions* and has many applications. Ions conduct electricity through the solution but oxidation and reduction of the ions takes place at the electrodes in an electrochemical cell. An electrochemical cell consists of two metallic electrodes dipping in electrolytic solution(s). Electrochemical cells are of two types. In galvanic cell, the chemical energy of a spontaneous reaction is converted into electrical work, whereas in electrolytic cell, electrical energy is used to carry out a non-spontaneous reaction. The standard electrode potential for any electrode dipping in an appropriate solution is defined with respect to standard electrode potential of hydrogen electrode taken as zero. The standard potential of the cell can be obtained by taking the difference of the standard potentials of cathode and anode ($E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$). The standard potential of the cells are related to standard Gibbs energy ($\Delta_r G^\ominus = -nFE^\ominus$) and equilibrium constant ($\Delta_r G^\ominus = -RT \ln K$) of the reaction taking place in the cell. Concentration dependence of the potentials of the electrodes and the cells are given by Nernst equation. Batteries and fuel cells are very useful form of galvanic cell. Corrosion of metals is essentially an electrochemical phenomenon.

EXERCISES

5.1 Explain with examples the terms weak and strong electrolytes. How can these be distinguished?

5.2 Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

5.3 The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1}. Calculate its molar conductivity.

5.4 How much charge is required for the following reduction of
(i) 1 mol of Al^{3+} to Al.
(ii) 1 mol of Cu^{2+} to Cu.
(iii) 1 mol of MnO_4^- to Mn^{2+}

5.5 How much electricity in terms of Faraday is required to produce
(i) 20.0 g of Ca from molten $CaCl_2$
(ii) 40.0 g of Al from molten Al_2O_3.

5.6 How much electricity is required in coulomb for the oxidation of
(i) 1 mol of H_2O to O_2
(ii) 1 mol of FeO to Fe_2O_3.

5.7 A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

5.8 Three electrolytic cells A,B,C containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B . How long did the current flow? What mass of copper and of zinc were deposited?

5.9 Using the standard electrode potentials given in the Table 5, predict if the reaction between the following is feasible:
(a) $Fe^{3+}(aq)$ and $I^-(aq)$
(b) $Ag^+(aq)$ and Cu(s)
(c) $Fe^{3+}(aq)$ and $Br^-(aq)$
(d) Ag(s) and $Fe^{3+}(aq)$
(e) $Br_2(aq)$ and $Fe^{2+}(aq)$.

5.10 Predict the products of electrolysis in each of the following:
(i) An aqueous solution of $AgNO_3$ with silver electrodes
(ii) An aqueous solution of $AgNO_3$ with platinum electrodes
(iii) A dilute solution of H_2SO_4 with platinum electrodes
(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

5.11 Arrange the following metals in the order in which they displace each other from the solution of their salts.
Al, Cu, Fe, Mg and Zn.

5.12 Given the standard electrode potentials,
$K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$,
$Hg^{2+}/Hg = 0.79V$
$Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74V$
Arrange these metals in their increasing order of reducing power.

5.13 Depict the galvanic cell in which the reaction $Zn(s)+2Ag^+(aq) \rightarrow Zn^{2+}(aq)+2Ag(s)$ takes place. Further show:
(i) Which of the electrode is negatively charged
(ii) The carriers of the current in the cell
(iii) Individual reaction at each electrode.

5.14 Calculate the standard cell potentials of galvanic cell in which the following reactions take place:
(i) $2Cr(s) + 3\ Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd$
(ii) $Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$
Calculate the $\Delta_r G^\ominus$ and equilibrium constant of the reactions.

5.15 Write the Nernst equation and e.m.f. of the following cells at 298 K:
(i) $Mg(s)|Mg^{2+}(0.001M)||Cu^{2+}(0.0001\ M)|Cu(s)$
(ii) $Fe(s)|Fe^{2+}(0.001M)||H^+(1M)|H_2(g)(1bar)|\ Pt(s)$
(iii) $Sn(s)|Sn^{2+}(0.050\ M)||H^+(0.020\ M)|H_2(g)\ (1\ bar)|Pt(s)$
(iv) $Pt(s)|Br_2(l)|Br^-(0.010\ M)||H^+(0.030\ M)|\ H_2(g)\ (1\ bar)|Pt(s)$.

5.16 In the button cell widely used in watches and other devices the following reaction takes place:
$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$
Determine $\Delta_r G^\ominus$ and $E^\ominus$ for the reaction.

5.17 The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}.

5.18 The conductivity of sodium chloride at 298 K has been determined at different concentration and the results are given below:

Concentration/M	0.001	0.010	0.020	0.050	0.100
$10^2 \times \kappa$/S m^{-1}	1.237	11.85	23.15	55.53	106.74

Calculate Λ for all concentrations and draw a plot between Λ and $c^{1/2}$. Find the value of Λ^0.

5.19 Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity and if Λ^0 for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?

UNIT 6

CHEMICAL KINETICS

OBJECTIVES

After studying this Unit, you will be able to:

- define the average and instantaneous rate of a reaction and express it in terms of change in concentration of either of the reactants or products with time.
- distinguish between elementary (one step) and complex reactions (multiple steps).
- describe the molecularity of elementary reactions and order of simple and complex reactions.
- define rate constant and describe the dependence of the rate of reaction on the concentration of the reactants.
- describe methods for determining the rate constant of zeroth and first order reactions.
- define half life time of a reaction and correlate it with rate constant and initial concentration of one of the reactants.
- describe the temperature dependence of rate constant in terms of Arrhenius equation.
- learn the physical meaning of activation energy and pre-exponential factor.
- describe the mechanism of some simple reactions.

"One of the main aims of chemistry is to understand how chemical reactions occur."

As chemists we are interested in different aspects of a chemical reaction. First of all we want to know if a reaction represented by a chemical equation is feasible or not i.e. under the given experimental conditions, is it possible at all to convert the reactants into the products? The answer to this question has already been given in Unit 4, where the criteria for the feasibility of a process under given experimental conditions have been laid out. At constant temperature and pressure, a reaction is possible only if it is accompanied by decrease in Gibbs energy. If the reaction is feasible then we want to know to what extent or how far this reaction will proceed. We have already discussed in (Class XI, Unit 7) that this question can be answered if we know the equilibrium constant of the reaction.

The third question is about the speed with which the reactants are converted into products i.e., how fast a reaction can occur? Although thermodynamics answers the first two questions satisfactorily, it cannot answer the third question at all. The branch of science called **Chemical kinetics** deals with the rate of reactions and the factors that influence the rate of a reaction. The factors are nature of the reactants, concentration of reactants, products and catalysts besides the temperature and pressure at which the reaction is carried out. The rates of reactions are affected by light, and also by electric and magnetic fields. Since industrial scale production requires quick and economic manufacturing of desired products without leading to any side reactions; the knowledge about the kinetics of the reaction helps to optimise the conditions of the reaction under which it should be carried out. It also deals with the reaction mechanism i.e., how the atoms

rearrange themselves in the reactant molecules in a single step or a number of steps, finally leading to the product molecules. Chemical kinetics is a vast subject and in this Unit we shall study only some elementary and basic aspects of the subject.

6.1 RATE OF CHEMICAL REACTION

The progress of chemical reactions is monitored by measuring the concentration(s) of reactants and/or products as a function of time. Here we assume that volume of the system remains constant and there is no removal from or addition to the reaction vessel of any of the reactants or products. Under such conditions we find that during the course of a reaction the concentration of the reactants decreases while that of products increases. We define rate of a reaction in such a manner that it is always a positive quantity. In the reaction:

$R \rightarrow P$ (6.1)

one mole of the reactant 'R' produces one mole of the product 'P'. The changes in the concentration of R and P with time, are therefore, equal in magnitude but have opposite sign. The plots of the concentrations of R and P as a function of time t are shown in Fig. 6.1. If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their respective concentrations at time t_2, then

$\Delta t = t_2 - t_1$, $\Delta[R] = [R]_2 - [R]_1$ and

$\Delta[P] = [P]_2 - [P]_1$, where Δ [R] and (6.2)

$\Delta[P]$ are the changes in concentrations of R and P during the time interval Δt.

The average rate of the reaction, r_{av}, is given by the equation:

$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \quad (6.3)$$

It may be noted from eq. 6.3 that the dimensions of rate are concentration/time. Units of time and concentration can be chosen according to the convenience of the experimentalist.

Like average rate of a reaction, it is well known that average speed of a car can be easily calculated by knowing the distance (s) covered by it in time (t). For example, if the car covers 240 km in 4 hours, its average speed = s/t = 240km/4hr = 60km/hr. However, during the journey the driver can look from the speedometer that the speed keeps on changing depending on

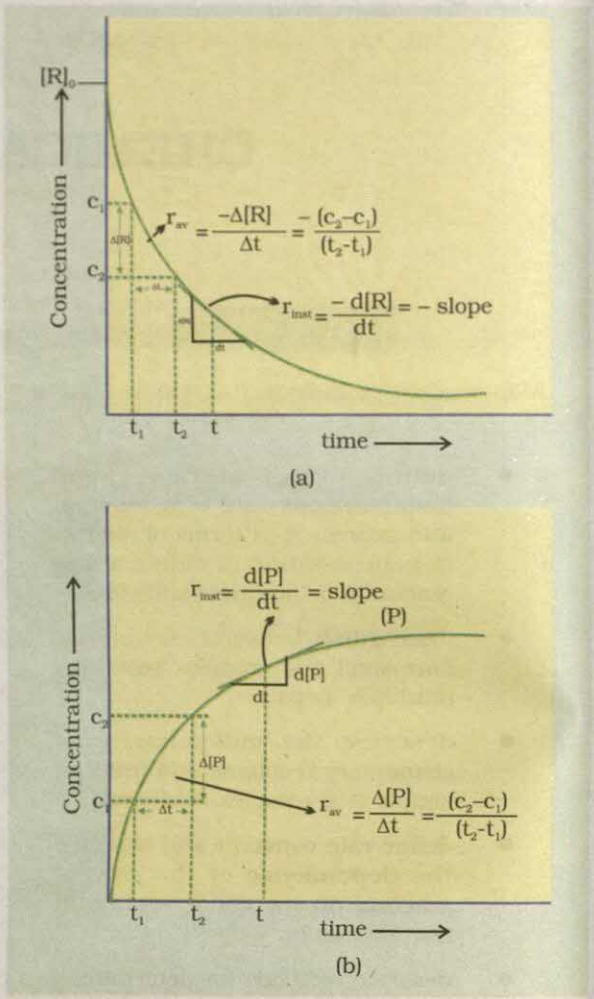


Fig. 6.1 *Instantaneous and average rate of a reaction.*

the condition of the road, traffic density and weather etc. The needle of the speedometer indicating instantaneous speed may vary from as low as 10 km/hr to 120 km/hr. For a chemical reaction the average rate depends on the values of t_2 and t_1 chosen. Initially the rate is very fast and later on the rate decreases. Like instantaneous speed the instantaneous rate, r_{inst} also changes and the instantaneous rate has to be at a particular instant (time t). Mathematically we represent instantaneous rate by:

$$\frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \text{ or } r_{inst} = \frac{-d[R]}{dt} = \frac{d[P]}{dt} \quad (6.4)$$

as $\Delta t \rightarrow 0$

It may be noted that instantaneous rate can be determined by drawing a tangent at time t on either of the curves for concentration of

R and P versus time, t. The slope of the curve at time t is related to the instantaneous rate by the equation:

r_{inst} = – slope (for R) = $-d[R]/dt$ or
= slope (for P) = $d[P]/dt$

Example 6.1

From the concentrations of R at different times given below, calculate the average rate of the reaction: R → P during different intervals of time.

t/s	0	5	10	20	30
$10^3 \times$ [R]/mol L^{-1}	160	80	40	10	2.5

Solution

We can determine the difference in concentration over different intervals of time and thus determine the rate by dividing Δ[R] by Δt

$[R]_1 \times 10^3$ / mol L^{-1}	$[R]_2 \times 10^3$ / mol L^{-1}	t_2 / s	t_1 / s	$r_{av} \times 10^3$ / mol $L^{-1} s^{-1}$ $= \frac{[R_2 - R_1] \times 10^3}{[t_2 - t_1]}$
160	80	5	0	16
80	40	10	5	8
40	10	20	10	3
10	2.5	30	20	0.75

It can be seen that the average rate falls from 16×10^{-3} mol L^{-1} s^{-1} to 0.75×10^{-3} mol L^{-1} s^{-1} during the time interval 0 to 30s. If we want to determine the instantaneous rate of reaction, we draw a plot between concentration and time and determine the rate at any given time from the slope at the desired time 't'

At t = 5 s $r_{inst} = 7.20 \times 10^{-3}$ mol L^{-1} s^{-1}
At t = 10 s $r_{inst} = 5.60 \times 10^{-3}$ mol L^{-1} s^{-1}
At t = 20 s $r_{inst} = 1.40 \times 10^{-3}$ mol L^{-1} s^{-1}
At t = 30 s $r_{inst} = 0.35 \times 10^{-3}$ mol L^{-1} s^{-1}

We have just considered a reaction in which one mole of the reactant gives one mole of the product. In general, stoichiometric coefficients of the reactants and products are not unity nor are they equal to each other. For example, in the reaction:

$$2\,NO\,(g) + O_2\,(g) \rightarrow 2\,NO_2\,(g) \qquad (6.5)$$

two moles of NO react with one mole of O_2 to produce two moles of NO_2. This means the rate of change of concentration of NO is twice that of O_2 and equal and opposite to the rate of change of concentration of NO_2. The rate of reaction can be monitored by determining the rate of change of concentration of either of the reactants or products but to be consistent, the following convention has been adopted:

Rate of Reaction = $-1/\upsilon_R\,(d[R]/dt)$
$= 1/\upsilon_P\,(d[P]/dt)$ (6.6)

where R is any one of the reactants whose stoichiometric coefficient in the chemical equation is υ_R and P is one of the products whose stoichiometric coefficient is υ_P.

In the above example, the stoichiometric coefficients of NO, O_2 and NO_2 are 2, 1 and 2 respectively and hence the rate is given by

$$\text{Rate} = -\frac{1}{2}\frac{d[NO]}{dt} = \frac{-d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} \qquad (6.7)$$

Similarly for the reaction

$$5\,Br^-(aq) + BrO_3^-(aq) + 6\,H^+(aq) = 3\,Br_2(aq) + 3\,H_2O(l) \qquad (6.8)$$

$$\text{rate} = \frac{-1}{5}\frac{d[Br^-]}{dt} = \frac{-d[BrO_3^-]}{dt}$$

$$= \frac{-1}{6}\frac{d[H^+]}{dt} = \frac{1}{3}\frac{d[Br_2]}{dt} \qquad (6.9)$$

In aqueous solution change in concentration of water is very small and hence we do not use change in concentration of water for expressing the rate.

Example 6.2

The decomposition of N_2O_5 in CCl_4 solution at 318 K has been studied by monitoring the concentration of N_2O_5 in the solution. Initially the concentration of N_2O_5 is 2.33 M and after 184 minutes, it is reduced to 2.08 M. The reaction takes place according to the equation:

$$2\,N_2O_5 \longrightarrow 4NO_2 + O_2$$

Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of NO_2 during this period?

Solution

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = -\frac{1}{2}\frac{[2.08 - 2.33]\,\text{mol}\,L^{-1}}{184\,\text{min}}$$

$$= 6.79\times10^{-4}\ \frac{\text{mol L}^{-1}}{\text{min}} = 6.79\times10^{-4}\ \frac{\text{mol L}^{-1}}{\text{min}} \times \frac{60\text{min}}{1\text{hr}}$$

$$= 4.07\times10^{-2}\ \frac{\text{mol L}^{-1}}{\text{hr}}$$

$$= 6.79\times10^{-4}\ \frac{\text{mol L}^{-1}}{\text{min}} \times \frac{1\text{min}}{60\text{s}}$$

$$= 1.13\times10^{-5}\ \frac{\text{mol L}^{-1}}{\text{s}}$$

It may be remembered that

$$\text{Rate} = \frac{1}{4}\ \frac{d[NO_2]}{dt}$$

$$\frac{d[NO_2]}{dt} = 6.79\times10^{-4}\times4\ \frac{\text{mol L}^{-1}}{\text{min}} = 2.72\times10^{-3}.\frac{\text{mol L}^{-1}}{\text{min}}.$$

Example 6.3

The concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes for the reaction R → P. Calculate the average rate of reaction using units of time both in minutes and seconds.

Solution

$$\text{rate} = \frac{-\Delta[R]}{\Delta t} = \frac{-[0.02M - 0.03M]}{25\,\text{min}}$$

$$= 0.01/25\,\text{mol L}^{-1}\text{min}^{-1} = 0.4 \times 10^{-3}\ \text{mol L}^{-1}\ \text{min}^{-1}$$

$$= 0.4 \times 10^{-3}\ \text{mol L}^{-1}\ \text{min}^{-1}\ \text{min}\ /60\ \text{s}$$

$$= 0.066 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1} = 6.6 \times 10^{-6}\ \text{mol L}^{-1}\ \text{s}^{-1}.$$

For a gaseous reaction at constant T, concentration is directly proportional to the partial pressure of a species and hence rate can also be expressed as rate of change in partial pressure of the reactant or product.

6.1.1 Dependence of Rate on Concentration of Reactants

The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and sometimes even on the concentration of the products or some foreign substances. The representation of rate of a reaction in terms of the concentration of the reactants is called **rate law**. The rate law for a given reaction is established by experimental study of the rate of reaction over a wide range of concentration of the reactants and products. The rate law thus established is also called **differential rate equation or rate expression.**

Generally, the rate law expressions are not simple. These may differ even for the same reaction depending on the condition under which the reaction has been carried out. For example, for the reaction:

$H_2\,(g) + I_2\,(g) \rightarrow 2HI(g)$ (6.10)

$\text{Rate} = k\,[H_2]\,[I_2]$ (6.11)

While for a similar type of reaction:

$H_2\,(g) + Br_2\,(g) = 2HBr(g)$ (6.12)

$$\text{Rate} = \frac{k_a\,[H_2][Br_2]^{1/2}}{1 + k_b\,[HBr/Br_2]} \quad (6.13)$$

Here k_a and k_b are constants and depend on temperature of the reaction. It can be seen that in the absence of HBr, the initial rate of reaction (6.13) is given by the equation:

$\text{Rate} = k_a\,[H_2]\,[Br_2]^{1/2}$ (6.14)

Sometimes, the rate equation has more than one term on the right hand side, especially when a number of parallel reactions take place simultaneously.

6.1.2 Rate Constant and Order of a Reaction

For a large number of reactions starting with pure reactants we obtain simple rate equation in which rate is proportional to the concentration of the reactants raised to some power. For example, for the reaction (6.10) rate is proportional to the concentration of hydrogen and iodine while in reaction (6.12) the rate is proportional to the concentration of hydrogen and square root of the concentration of bromine when HBr is not present in the system.

In example 6.2, in the decomposition of N_2O_5, it has been found experimentally that the rate of the reaction is directly proportional to the concentration of dinitogen pentaoxide i.e.,

$$\text{Rate} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} \propto [N_2O_5]$$

$$\text{or} \quad -\frac{1}{2}\frac{d[N_2O_5]}{dt} = k[N_2O_5] \quad (6.15)$$

The constant of proportionality, k, is called the **rate constant** or **specific rate constant** since it is the rate of reaction when the concentration of $[N_2O_5]$ is unity i.e. 1M. It is obvious that the rate of the reaction is directly proportional to the concentration of $[N_2O_5]$ or

the first power of the concentration. The power of the concentration of the reactant in the above rate law is called the **order of the reaction with respect to that reactant** and in this case it is a **first order reaction.**

It may be noted that the power of the concentration (i.e., order of the reaction) has nothing to do with the value of stoichiometric coefficient of the reactant. In this case, it can be seen that the stoichiometric coefficient of N_2O_5 is 2 while the order of reaction is 1.

For the general reaction:

$$\nu_A A + \nu_B B \ldots = \nu_L L + \nu_M M \ldots \quad (6.16)$$

if the experimentally determined rate law is given by the equation:

$$\text{rate} = k [A]^a [B]^b \ldots\ldots \quad (6.17)$$

then we can say that the reaction is of a^{th} order in A and of b^{th} order in B and the overall order of the reaction is the sum of the exponents of concentrations of all the reactants in the rate equation.

Thus, in the reaction,

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+ \rightarrow 3Br_2(aq) + 3H_2O(l) \quad (6.18)$$

experimentally determined rate law is given by the equation:

$$\text{Rate} = k [Br^-] [BrO_3^-] [H^+]^2 \quad (6.19)$$

We note that the reaction is first order in $[Br^-]$ and $[BrO_3^-]$ and second order in $[H^+]$ and the overall order of the reaction is 1+1+2= 4.

The overall order of the reaction may be zero or even a fraction, say, 0.5. We can now define **that the order of a reaction with respect to a reactant is the power (exponent) of the concentration of the reactant to which the rate of the reaction is directly proportional. The overall order of the reaction is the sum of the exponents of all the reactants in the rate expression.**

It may be noted that reaction (6.18) does not take place in one single step. It is almost impossible for all the 12 molecules of the reactants to be in a state of encounter simultaneously. Such a reaction is called **complex reaction** and takes place in a sequence of a number of **elementary reactions**. In an elementary reaction, the reaction takes place in one step. The reaction between H_2 and I_2 is an elementary reaction[1] as H_2 and I_2 molecules collide together and separate out as 2HI molecule.

On the other hand, the reaction between H_2 and Br_2 is a complex reaction that takes place in a number of steps involving both Br and H atoms.

The definition of order of reaction is valid both for elementary and complex reactions and the order of a reaction has always to be determined experimentally.

We have noted earlier that the dimensions of rate are equal to concentration/time. The SI units for concentration are mol/m^3, mol/dm^3 or mol/L and seconds for time but other units are used depending on how fast or slow is the reaction. For very slow reactions, time may be chosen in years and for very fast reactions it may be chosen in nano (10^{-9}) or pico (10^{-12}) second.

From Eq. (6.17) it can be seen that the rate constant may be written as

$$k = \frac{\text{rate}}{[A]^a [B]^b} \quad (6.20)$$

If a+b.... = n, i.e., the overall order of the reaction is n, then the dimensions of rate constant depend on the order of the reaction. Thus, the dimensions of k are equal to

$$\frac{\text{Concentration}}{\text{time}\times[\text{concentration}]^n} = [\text{concentration}]^{1-n}[\text{time}]^{-1}$$

If we choose concentration in molarity and time in second, then for

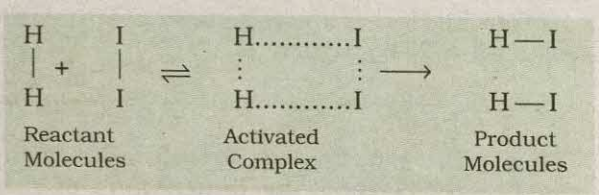
n=0 zero order reaction	k has the units	$mol\ L^{-1}\ s^{-1}$
n=1 first order reaction	k has the units	s^{-1}
n=2 second order reaction	k has the units	$(mol/\ L)^{-1}s^{-1}$
n=n nth order reaction	k has the units	$(mol/\ L)^{(1-n)}s^{-1}$

It is obvious that rate constant has higher magnitude when larger unit of time is chosen. We already know [Unit 1, Class XI] how to convert the units of a given physical quantity.

We have mentioned that the order of a reaction has to be determined experimentally. On the other hand, **molecularity of a reaction** can be

[1] *At high temperature and in presence of light, the reaction is no longer an elementary reaction and involves iodine atoms.*

defined only for an elementary reaction. **Molecularity has no meaning for a complex reaction**. For an elementary reaction it can be defined as the number of reactant molecules which come together before conversion into product molecules. For bimolecular and ter-molecular elementary reactions, the order of reaction is the same as its molecularity and order with respect to each reactant is equal to its stoichiometric coefficient in the chemical equation representing the elementary reaction. Thus, the molecularity of reaction between H_2 and I_2 is two as one molecule of hydrogen and one molecule of iodine come together to form the activated complex which separates into two HI molecules according to the following scheme:



The order of reaction with respect to both hydrogen and iodine is unity and the overall order of the reaction is equal to two which is equal to the molecularity of the reaction. For uni-molecular elementary reactions, the order of reaction as expected is one at high pressure or concentration. At low pressure, the reaction becomes second order but then it is no longer an elementary reaction and the reaction takes place in 3 steps and hence becomes a complex reaction for which molecularity cannot be defined.

6.1.3 Integrated Rate Equations

We have already noted that the concentration dependence of rate is called differential rate equation. It is not always convenient to determine the instantaneous rate, as it is measured by determination of slope of the tangent at point 't' in the concentration versus time curve (Fig. 6.1). This makes it difficult to determine the rate law and hence the determination of the order of the reaction. In order to avoid this difficulty, we can integrate the rate equation and obtain integrated rate equation that gives a relation between directly measured experimental quantities i.e., concentrations at different times. The integrated rate equations are different for reactions of different orders. Here we shall derive these equations only for zero and first order reactions.

Zero Order Reaction

Zero order reaction means that the rate of the reaction is proportional to the zero power of the concentration of the reactant, R in the reaction:

$$R \rightarrow P$$

However, any quantity raised to the power zero is unity. This implies that the rate of reaction is constant and is equal to the zero order rate constant.

$$\text{rate} = \frac{-d[R]}{dt} = k[R]^0 = k \quad \text{or} \qquad (6.21)$$

$$d[R] = kdt$$

Now simple integration gives us

$$[R] = -kt + \theta \qquad (6.22)$$

Here θ is the constant of integration and can be determined from our knowledge that at $t = 0$, the concentration of $R = [R]_0$ or the initial concentration of reactant. Thus

$$[R]_0 = -k \times 0 + \theta \quad \text{or} \quad [R]_0 = \theta$$

Substituting the value of θ in eq. 6.22 we obtain

$$[R] = -kt + [R]_0 \qquad (6.23)$$

It can be seen that if we draw a plot between [R] and t we get a straight line (Fig. 6.2) with slope = –k and intercept equal to $[R]_0$

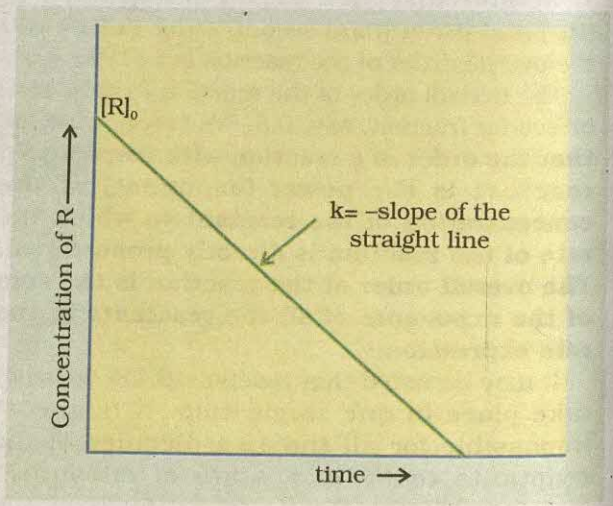


Fig. 6.2 *Variation in the concentration of a reactant with time in a zero order reaction.*

Alternatively rate constant k can be determined from the eq. [6.23] if we know the concentration of R at any time t and $[R]_0$. Thus,

$$k = \frac{[R]_0 - [R]_t}{t} \qquad (6.24)$$

The time required to reduce the initial concentration of the reactant to half of its initial value is called **half life time** or **half life period** and is denoted by $t_{1/2}$. We can see from Eq. (6.24), that for a zero order reaction $t_{1/2}$ is given by the relation:

$$t_{1/2} = \frac{[R]_0 - 1/2[R]_0}{k} = \frac{[R]_0}{2k} \qquad (6.25)$$

Thus, we note that for zero order reaction $t_{1/2}$ is directly proportional to the initial concentration of the reactant and inversely proportional to the rate constant.

Zero order reactions generally take place in a heterogeneous system. In such a system, the reactant is adsorbed on the surface of a solid catalyst (where it is converted into product) (Unit 7). The fraction of the surface of the catalyst covered by the reactant is proportional to its concentration at low values and the rate of the reaction is first order. However, after certain concentration limit of the reactant, the surface of the catalyst is fully covered and any further increase of concentration of the reactant does not change the situation and the reaction rate becomes independent of concentration and it becomes a zero order reaction. For example, the decomposition of NH_3 on finely divided platinum surface is first order when the pressure (concentration) of NH_3 in the system is low. At higher concentration when the surface of the catalyst (finely divided platinum) is fully covered with layer of NH_3 molecules, the reaction becomes zero order. In general, the rate of the reaction is given by the equation:

$$\text{rate} = \frac{k_1[NH_3]}{1+k_2[NH_3]} \qquad (6.26)$$

Here k_1 and k_2 are constants. When $[NH_3]$ is very low, $k_2[NH_3]$ can be neglected compared to unity and we have:

rate $= k_1 [NH_3]$ and the reaction is first order in ammonia.

At higher concentration of ammonia, we may neglect 1 compared to $k_2[NH_3]$ and Eq. (6.26) reduces to:

$$\text{rate} = \frac{k_1[NH_3]}{k_2[NH_3]} = \frac{k_1}{k_2} = k \qquad (6.27)$$

It can be seen that the rate is constant, a characteristic of zero order reaction.

First Order Reaction

In this class of reactions, the rate of reaction is proportional to the first power of the concentration of the reactant R. For example, in the reaction:

$$R \rightarrow P$$

$$\text{rate of reaction} = \frac{-d[R]}{dt} = k[R]$$

$$\text{or } \frac{-d[R]}{[R]} = k\,dt$$

On integration we get

$$\ln [R] = -kt + \theta \qquad (6.28)$$

Where θ is the constant of integration and can be determined from our knowledge that at $t = 0$, $[R] = [R]_0$, i.e.,

$$\ln [R]_0 = -k \times 0 + \theta \text{ or } \theta = \ln [R]_0$$

Putting the value of θ in eq. 6.28, we obtain

$$\ln[R] = -kt + \ln [R]_0 \qquad (6.29)$$

Eq. 6.29 can also be written as

$$k = (1/t) \ln \{[R]_0/[R]\} \qquad (6.30)$$

$$k = 1/(t_2 - t_1) \ln \{[R]_1/[R]_2\} \qquad (6.31)$$

where $[R]_1$ and $[R]_2$ are the concentrations of the reactant at time t_1 and t_2 respectively. The Eq. (6.29) can also be written in the following exponential form,

$$[R] = [R]_0 e^{-kt} \qquad (6.32)$$

It can be seen from the Eq. (6.29) that if we draw ln [R] against t, we get a straight line [Fig. 6.3] with slope = –k and intercept equal to $\ln[R]_0$. The value of k can also be determined from Eq. (6.31) if we know the concentration of the reactant at two different values of t. Eq. (6.32) suggests that concentration of the reactant decreases exponentially with time t.

All natural and artificial radioactive decay of nuclei takes place by first order reaction (Unit 11). The half life period can be derived from the Eq. [6.30]as at $t_{1/2}$, $[R]_{t_{1/2}} = \frac{1}{2}[R]_0$ and we have:

$$t_{1/2} = \frac{1}{k} \ln \left\{ \frac{[R]_0}{1/2[R]_0} \right\} = \frac{\ln 2}{k} = \frac{0.69}{k} \qquad (6.33)$$

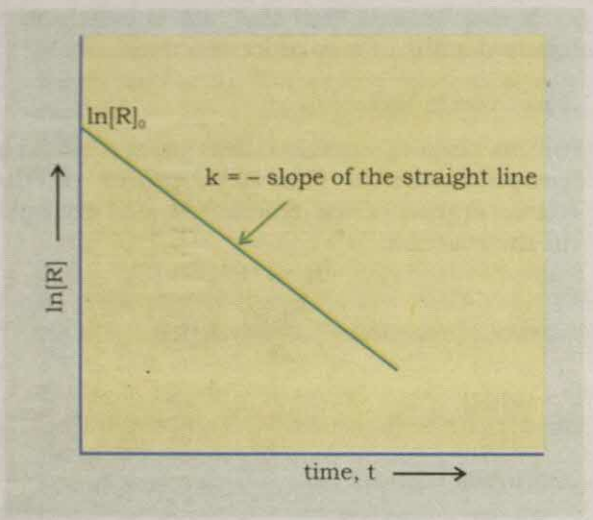


Fig. 6.3 *A plot between ln[R] and t gives a straight line with slope equal to –k.*

It can be seen that $t_{1/2}$ for the first order reaction is independent of initial concentration and inversely proportional to the rate constant.

Many radioactive decay processes are characterised by their $t_{1/2}$ values. We can determine the age of rocks or age of an old artefact by using half life period of suitable radioactive isotope of the element present in the article (Unit 11).

Pseudo First Order Reaction

Some reactions are first order each with respect to two different reactants i.e.,

rate = k [A][B]

However, if one of the reactants is the solvent (that is always present in high concentration) then there is very little change in its concentration and it practically remains constant during the course of reaction. For example, if [A] = 0.01M and [B] = 55.5 M, the concentration of B changes from 55.5 to 55.49 M even after the completion of the reaction. Under such condition, we may write the above equation as

rate = k_0 [A] , where k_0 = k [B]

This now behaves as a first order reaction in A. Such reactions are known as **pseudo first order reactions**. For example, during the hydrolysis of ethyl acetate into ethyl alcohol and acetic acid, the concentration of water is so large that it practically remains constant. Therefore, the hydrolysis of ethyl acetate is pseudo first order in ethyl acetate in aqueous solution.

Example 6.4

Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of the ester at different times is given below:

t/min	0	30	60	90
c/M	0.8500	0.8004	0.7538	0.7096

Show that it follows a pseudo first order reaction as the concentration of H_2O remains nearly constant (51.2 M) during the course of the reaction. What is the value of k in this equation?

rate = k $[CH_3COOCH_3][H_2O]$

Solution

For pseudo first order reaction, the reaction should be first order with respect to ester when $[H_2O]$ = constant.

From the above data we note

t	c	$\left[k[H_2O] = \frac{\ln (c_0/c)}{t}\right]/\text{min}$
0	0.8500	–
30	0.8004	2.004×10^{-3}
60	0.7538	2.002×10^{-3}
90	0.7096	2.005×10^{-3}

It can be seen that k $[H_2O]$ is constant and equal to 2.004×10^{-3} min and hence it is pseudo first order reaction. We can now determine k from

$k[H_2O] = 2.004 \times 10^{-3}\ min^{-1}$

$k[51.2\ M] = 2.004 \times 10^{-3}\ min^{-1}$

$k = 3.914 \times 10^{-5}\ M^{-1}min^{-1}$

It has the units of a second order rate constant.

6.1.4 Determination of Order of Reaction

There are several methods available for determining the order of a reaction. All these methods are based on the use of differential or integral rate equations given in the previous section.

1. Initial Rate Method

In this method, the initial rate of a reaction is determined by varying the concentration of one of the reactants while others are kept constant. The initial rate r_0 is determined either numerically or from the slope of the curve vs time at time t = 0.

Thus, initial rate of the reaction is given by

r_0 = rate = $k\,[A]_0^a\,[B]_0^b\,[C]_0^c$ (6.34)

If [B] and [C] are kept constant, then

$r_0 = k_0\,[A]_0^a$ where $k_0 = k\,[B]_0^b\,[C]_0^c$ (6.35)

The value of 'a' can be determined by inspecting the rate at different values of [A]. Alternatively, if we know the initial rates at two different concentrations of A, we have

$(r_0)_1 = k_0\,\{([A]_0)_1\}^a$ (6.36)

$(r_0)_2 = k_0\,\{([A]_0)_2\}^a$ (6.37)

where $(r_0)_1$ and $(r_0)_2$ are the initial rates of reaction when initial concentration of A are $[A_0]_1$ and $[A_0]_2$ respectively. Dividing eq. (6.36) by Eq. (6.37) we get

$(r_0)_1/(r_0)_2 = \{([A]_0)_1\}^a/\{([A]_0)_2\}^a$ (6.38)

Taking log on both sides we obtain

$$\log[(r_0)_1/(r_0)_2] = a \log\{([A]_0)_1\}/\{([A]_0)_2\}$$

$$a = \frac{\log[(r_0)_1/(r_0)_2]}{\log\{([A]_0)_1/([A]_0)_2\}} \quad (6.39)$$

Thus the order of reaction with respect to A can be determined. In the same manner, the order of reaction with respect to other reactants can also be determined and the overall order of the reaction is the sum of all the exponents in Eq. [6.34]

i.e. order of reaction, n = a + b + c....

Example 6.5

The rates of a reaction starting with initial concentrations 2×10^{-3} M and 1×10^{-3} M are equal to 2.40×10^{-4} M s^{-1} and 0.60×10^{-4} M s^{-1} respectively. Calculate the order of the reaction with respect to the reactant and also the rate constant.

Solution

$r_0 = k[A_0]^a$

$$\frac{(r_0)_1}{(r_0)_2} = \left\{\frac{([A]_0)_1}{([A]_0)_2}\right\}^a$$

$$a = \frac{\log[(r_0)_1/(r_0)_2]}{\log\{([A]_0)_1/([A]_0)_2\}} = \frac{\log(2.40\times10^{-4}/0.60\times10^{-4})}{\log(2\times10^{-3}/1\times10^{-3})}$$

$= \log 4/\log 2 = 2$

Thus, reaction is of second order.

The rate constant k = rate/[A]^2

$= 2.4 \times 10^{-4}$ mol L^{-1} s^{-1}/ (2×10^{-3} mol L^{-1})^2

$= 0.6 \times 10^2$ $mol^{-1}L$ s^{-1}

Example 6.6

The initial rate of reaction:

A + 5B + 6C = 3L + 3M

has been determined by measuring the rate of disappearance of A under the following conditions:

Experiment No.	$[A]_0$ M	$[B]_0$ M	$[C]_0$ M	Initial rate M/min
I	0.02	0.02	0.02	2.08×10^{-3}
II	0.01	0.02	0.02	1.04×10^{-3}
III	0.02	0.04	0.02	4.16×10^{-3}
IV	0.02	0.02	0.04	8.32×10^{-3}

Determine the order of reaction with respect to each reactant and overall order of the reaction. What is the rate constant? Calculate the initial rate of the reaction when the concentration of all the reactants is 0.01M. Calculate the initial rate of change in concentration of B and L.

Solution

In experiments I and II, initial concentrations of B and C remain unchanged and hence from the rate expression

$r = k\,[A]_0^a\,[B]_0^b\,[C]_0^c = k_0\,[A]_0^a$,

$$\text{We get } \frac{(r_0)_1}{(r_0)_2} = \frac{2.08\times10^{-3}}{1.04\times10^{-3}} = \frac{\{([A]_0)_1\}^a}{\{([A]_0)_2\}^a} = \frac{0.02^a}{0.01^a}$$

or $2 = (2)^a$ and $a = 1$

Similarly

$$\frac{(r_0)_3}{(r_0)_1} = \frac{4.16\times10^{-3}}{2.08\times10^{-3}} = \frac{\{([B]_0)_3\}^b}{\{([B]_0)_1\}^b} = \frac{0.04^b}{0.02^b}$$

$2 = (2)^b$ or $b = 1$

and

$$\frac{(r_0)_4}{(r_0)_1} = \frac{8.32\times10^{-3}}{2.08\times10^{-3}} = \frac{\{([C]_0)_4\}^c}{\{([C]_0)_1\}^c} = \frac{0.04^c}{0.02^c}$$

or $4 = (2)^c$ and $c = 2$

Therefore, the order of the reaction with respect to A, B and C are 1, 1 and 2 respectively and the overall order of the reaction = 1+1+ 2 = 4

$$k = \frac{r}{[A]_0^a\,[B]_0^b\,[C]_0^c} = \frac{r}{[A]_0\,[B]_0\,[C]_0^2}$$

We can put the values from the set I,

$$k = \frac{2.08\times10^{-3}\ M\,min^{-1}}{16\times10^{-8}\ M^4} = 1.3 \times 10^4\ M^{-3}\ min^{-1}$$

rate of reaction when $[A]_0 = [B]_0 = [C]_0 = 0.01M$

$r = k[A]_0\,[B]_0\,[C]_0^2$

$= 1.3\times10^{4}\ M^{-3}\ min^{-1}\ [0.01M]\,[0.01M]\,[0.01M]^2$

$= 1.3 \times 10^{-4}\ M\ min^{-1}$

$$r = \frac{-1}{5}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[L]}{dt} = 1.3 \times 10^{-4}\ M\ min^{-1}$$

$$\frac{d[B]}{dt} = -5\times1.3\times10^{-4}\ M\ min^{-1} = -6.5\times10^{-4}\ M\ min^{-1}$$

$$\frac{d[L]}{dt} = 3\times1.3\times10^{-4}\ M\ min^{-1} = 3.9\times10^{-4}\ M\ min^{-1}$$

2. Use of Integrated Rate Equations

This method is also known as the method of trial and error. The kinetic data are fitted to different integrated rate equations. Wherever the data fit with the equation for the correct order of reaction, it will give constant value of rate constant for all data points (concentrations at different times). These equations also lead to straight lines when appropriate function of the concentration is plotted against time 't'. For example, for zero order reaction, a plot between concentration and time gives a straight line with slope of the line equal to –k. Similarly, for the first order reaction, a graph between ln[R] against t gives a straight line with slope equal to –k.

Example 6.7

The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different times and the results are given below:

t/s	0	100	200	300
p/Pa	4.00×10^3	3.50×10^3	3.00×10^3	2.5×10^3

Determine the order of reaction, its rate constant and half-life period.

Solution

It can be seen that rate of reaction between different time intervals is:

0-100s, $\text{rate} = -\dfrac{[3.50-4.00]\times10^3\text{Pa}}{100} = 5\ \text{Pa/s}$

100-200s, $\text{rate} = -\dfrac{[3.00-3.50]\times10^3\text{Pa}}{100\text{s}} = 5\ \text{Pa/s}$

200-300s, $\text{rate} = -\dfrac{[2.50-3.00]\times10^3\text{Pa}}{100} = 5\ \text{Pa/s}$

We notice that the rate remains constant and therefore, reaction is of zero order. Alternatively, if we plot p against t, it is a straight line again indicating it is a zero order reaction.

$k = \text{rate} = 5\ \text{Pa/s}$

$$t_{90\%} = \frac{\text{initial concentration or pressure}}{2k} \quad \text{(Eq. 6.25)}$$

$$= \frac{4.00\times10^3\text{Pa}}{2\times5\ \text{Pa s}^{-1}} = 400\text{s}$$

Example 6.8

The rate of decomposition of N_2O_5 in CCl_4 solution has been studied at 318 K and the following results have been obtained:

t/min	0	135	348	683	1680
c/M	2.08	1.91	1.67	1.35	0.72

Find the order of the reaction and calculate its rate constant. What is the half-life period?

Solution

It can be shown that the rate of the reaction does not remain constant with time and, therefore, it is not zero order reaction. We now try integrated first order equation i.e.,

$$k = \frac{\ln(c_0/c)}{t}$$

t/min	c/M	$k = \dfrac{\ln(c_0/c)}{t}$ min^{-1}
0	2.08	
135	1.91	6.30×10^{-4}
348	1.67	6.32×10^{-4}
683	1.35	6.32×10^{-4}
1680	0.72	6.31×10^{-4}

It can be seen that the value of k is almost constant for all the experimental results and hence it is first order reaction with $k = 6.31\times10^{-4}\ min^{-1}$.

$$t_{1/2} = \frac{0.69}{6.31\times10^{-4}\ min^{-1}} = 1.094 \times 10^3\ min^{-1}$$

Alternatively, if we draw a graph between ln c against t, we obtain a straight line with slope = – k.

3. Half-Life Method

The half-life period (time required to reduce the initial concentration to half its value) depends differently on the initial concentration of the

reactant for different order of reactions. Thus, we have:

For zero order reaction	$t_{1/2} \propto [R]_0$
For first order reaction	$t_{1/2}$ is independent of $[R]_0$
For second order reaction	$t_{1/2} \propto 1/[R]_0$
For n^{th} order reaction	$t_{1/2} \propto 1/[R]_0^{n-1}$

From the variation of $t_{1/2}$ with $[R]_0$ it becomes easy to find the order of the reaction.

4. Ostwald Isolation Method

Some reactions involve a large number of reactants. In order to determine the order of such reactions a method was developed by Ostwald also known as **isolation method**. In this method, the concentration of all the reactants are taken in large excess except that of one. The concentration change only for this reactant is significant as other are so much in excess that practically there is no change in their concentrations. The constant terms may be combined with the rate constant and we may write

$$\text{rate} = k[A]^a[B]^b[C]^c = k_0[A]^a \qquad (6.40)$$

The value of 'a' i.e. the order of reaction with respect to A can be determined by either of the methods (1-3) described above.

Example 6.9

The reaction:

$CH_3COF + H_2O = CH_3COOH + HF$

has been studied under the following initial conditions:

Case I		Case II	
$c^\circ_{H_2O}$	= 1.00M	$c^\circ_{H_2O}$	= 0.02M
$c^\circ_{CH_3COF}$	= 0.01M	$c^\circ_{CH_3COF}$	= 0.80M

Concentrations were monitored as a function of time and are given below:

Case I		Case II	
t/min	c_{CH_3COF} /M	t/min	c_{H_2O} /M
0	0.01000	0	0.0200
10	0.00857	10	0.0176
20	0.00735	20	0.0156
40	0.00540	40	0.0122

Determine the order of the reaction and the rate constant for the reaction.

Solution

Let rate $= k(c_{CH_3COF})^a (c_{H_2O})^b$

We shall use here Ostwald isolation method, as in one set of experimental conditions, $c^\circ_{H_2O} >> c^\circ_{CH_3COF}$ and in the second case, $c^\circ_{CH_3COF} >> c^\circ_{H_2O}$. In the first case we determine the order of the reaction with respect to CH_3COF. We note that the reaction is not of zero order as rate of reaction changes with time. We now apply first order equation and find,

t/min	c_{CH_3COF} /M	$\frac{k(c_{H_2O})^b}{\text{min}^{-1}} = \frac{\ln\left(\frac{c^0_{CH_3COF}}{c_{CH_3COF}}\right)}{t}$
0	0.01000	–
10	0.00857	0.0154
20	0.00735	0.0154
40	0.00540	0.0154

Therefore, $k(c_{H_2O})^b = 0.0154\ \text{min}^{-1}$

and we note the order of reaction with respect to CH_3COF is 1. Now we determine the order of reaction with respect to water. Again we try for first order equation.

t/min	c_{H_2O} /M	$\frac{k(c_{CH_3COF})^a}{\text{min}^{-1}} = \frac{\ln\left(\frac{c^0_{H_2O}}{c_{H_2O}}\right)}{t}$
0	0.0200	–
10	0.0176	0.0128
20	0.0156	0.0124
40	0.0122	0.0124

average $= 0.0125\ \text{min}^{-1}$

The reaction is first order in H_2O and we have

$k(c_{CH_3COF})^a = 0.0125\ \text{min}^{-1}$

Now in case I, $k = \frac{0.0154\ \text{min}^{-1}}{1.00\ \text{M}} = 0.0154\ \text{M}^{-1}\ \text{min}^{-1}$

and in case II, $k = 0.0125\ \text{min}^{-1}/0.800\ \text{M}$
$= 0.0156\ \text{M}^{-1}\ \text{min}^{-1}$.

6.2 THEORIES OF CHEMICAL KINETICS

We have already noted that a complex reaction involves a number of elementary steps. The mechanism of a reaction includes the sequence of elementary steps by which the reactant molecules are converted into products. The

necessary condition for any mechanism proposed is that the rate law expression derived on the basis of this mechanism should agree with the experimentally determined rate law. We do not have any general theory for rates of complex reactions. However, there have been several approaches to calculate the rate constant of elementary reactions. The elementary reactions may be unimolecular in which one molecule of the reactant is converted into the product(s). A bimolecular reaction may involve combinations of two molecules or exchange of atoms or group of atoms between the two reactant molecules. In a termolecular reaction, three reactant molecules take part in the reaction simultaneously. The temperature dependence of the rate constants for elementary reactions has helped a great deal in the development of various theories of reaction rates.

6.2.1 Temperature Dependence of Rate Constant

The rate constants for most of the reactions increase with the increase of temperature. It has been found that a plot of ln k against 1/T gives a straight line (Fig. 6.4) represented by the equation:

$$\ln k = \ln A - E_a/RT \qquad (6.41)$$

The equation is known as Arrhenius equation and can also be written as:

$$k = A\, e^{-E_a/RT} \qquad (6.42)$$

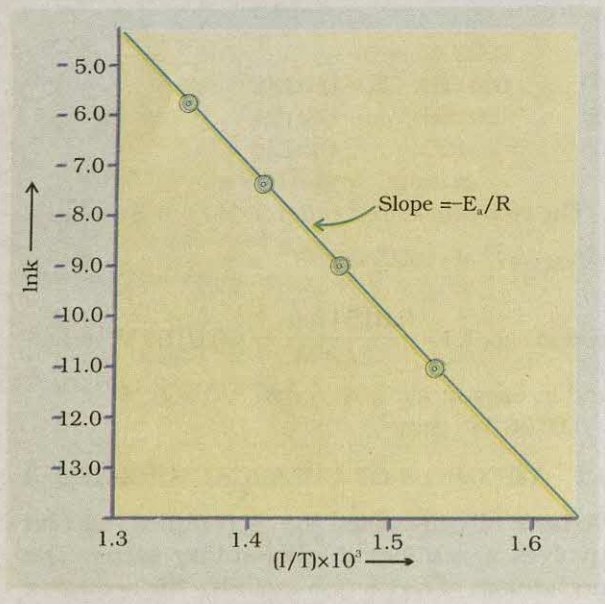


Fig. 6.4 *A plot between lnk and 1/T is a straight line with slope = $-E_a/R$.*

Eq. (6.42) tells us that the rate constant increases exponentially with the increase of temperature. How do we explain this exponential increase in the rate constant with increase in temperature? Is it due to increase in the average kinetic energy of the molecules? But we know that for the rise in temperature from 300 K to 310 K, the average kinetic energy of the molecules increases by 3% only (Unit 7, Class XI) as it is directly proportional to the temperature. On the other hand, for most reactions, the rate constant doubles i.e., increases by 100% for a 10°C rise near room temperature. This can be explained by assuming that certain threshold energy is required for the molecules to react. This is illustrated in (Fig. 6.5), where the fraction of the colliding molecules possessing different relative kinetic energies is plotted.

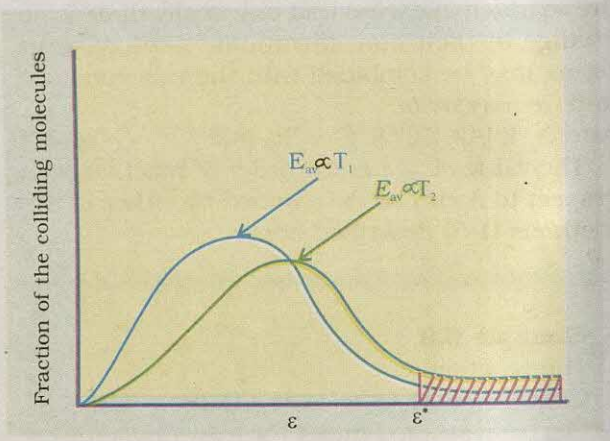


Fig. 6.5 *Distribution of relative kinetic energy of molecules in a gas.*

It can be seen that average relative kinetic energy increases as expected but population of colliding molecules (given by the shaded area under the curve) possessing the threshold relative kinetic energy, ε* increases considerably when temperature increases by 10 K. One may then relate E_a to threshold energy possessed by one Avogadro number of molecules, i.e.,

$$E_a = N_A\, \varepsilon^*$$

In Eq. (6.41) and (6.42), the parameter 'A' is called the pre-exponential factor or the frequency factor and has the units of the rate constant. The parameter E_a is called the activation energy. The two quantities 'A' and 'E_a' are collectively called the Arrhenius parameters. It may be noted from the Eq. (6.41) that ln A is the intercept

(i.e., the value at $1/T = 0$ or $T = \infty$) while $-E_a/R$ is the slope of the straight line drawn between ln k against $1/T$. In actual practice, the value of the parameter E_a is obtained from the slope ($E_a = -R \times$ slope) and the value of ln A is calculated from any value of ln k and $1/T$ on the straight line after the value of E_a has been calculated. The line cannot be extrapolated to $1/T = 0$ ($T = \infty$) as most reactions are studied only in a limited range of temperature. We can also calculate the value of A and E_a from known values of k at two different temperatures, i.e., put their values in Eq. (6.41) and solve the simultaneous equations:

$$\ln k_1 = \ln A - E_a/RT_1 \quad (6.43)$$

$$\ln k_2 = \ln A - E_a/RT_2 \quad (6.44)$$

Here k_1 and k_2 are the values of the rate constants at temperature T_1 and T_2 respectively. Subtracting eq. 6.43 from eq. 6.44 we obtain

$$\ln k_2 - \ln k_1 = E_a/RT_1 - E_a/RT_2$$

or $$\ln (k_2/k_1) = E_a/R\,[1/T_1 - 1/T_2] \quad (6.45)$$

Example 6.10

The rate constants of a reaction at 700 K and 760 K are 0.011 $M^{-1}s^{-1}$ and 0.105 $M^{-1}s^{-1}$ respectively. Calculate the values of Arrhenius parameters.

Solution

Putting the values of k and T in eq. 6.45 we obtain:

$$\ln (0.105\ M^{-1}\ s^{-1} / 0.011\ M^{-1}\ s^{-1}) = E_a/R\,[1/700\ K - 1/760\ K]$$

$$= E_a/R\,[60/700 \times 760]\ 1/K$$

$$E_a = \ln(0.105/0.011) \times \frac{700 \times 760}{60} K \times 8.314\ J\,mol^{-1}K^{-1}$$

$$= 166.310\ kJ/mol$$

Value of A can now be determined from

$$\ln A = \ln k + E_a/RT = \ln (0.011\ M^{-1}s^{-1}) + 166310\ J\ mol^{-1} / 8.314\ J\ mol^{-1}\ K^{-1} \times 700\ K$$

$$= 24.07 + \ln (M^{-1}\ s^{-1})$$

$$A = 2.8 \times 10^{10}\ M^{-1}s^{-1}.$$

Example 6.11

The values of rate constant for the decomposition of HI into I_2 and H_2 at different temperatures are given below

T/ K	633	667	710	738
10^4 k /$M^{-1}s^{-1}$	0.19	1.00	8.31	25.1

Draw a graph between ln k against $1/T$ and calculate the values of Arrhenius parameters.

Solution

Fig. 6.4 gives a plot between ln k against $1/T$. It can be seen that it is a straight line with slope = -20.62 K and therefore, its activation energy $E_a = -(-20.62\ K) \times 8.314\ J\ mol^{-1}\ K^{-1}$ $= 171400\ J\ mol^{-1}$ or $171.4\ kJ\ mol^{-1}$. We can now calculate the value of A from the value of k at 667 K :

$$\ln A = \ln k + E_a/RT = -9.2103 + \ln(M^{-1}s^{-1}) + 171400\ (J/mol)/8.314\ (J/mol\ K) \times 667K$$

$$= 21.695 + \ln(M^{-1}s^{-1})$$

$$A = 2.64 \times 10^9\ M^{-1}s^{-1}.$$

Example 6.12

The first order rate constant for the decomposition of ethyl iodide by the reaction:

$$C_2H_5I\ (g) \longrightarrow C_2H_4\ (g) + HI\ (g)$$

at 600K is $1.60 \times 10^{-5}\ s^{-1}$. Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700K.

Solution

We know that

$$\ln k_2 - \ln k_1 = E_a/R\,[1/T_1 - 1/T_2] \quad \text{or}$$

$$\ln k_2 = \ln k_1 + \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= \ln (1.60 \times 10^{-5}\ s^{-1}) + 209000\ J/mol \times \frac{\left[\frac{1}{600\ K} - \frac{1}{700\ K}\right]}{8.314 \times J/mol\ K}$$

$$\ln k_2 = \ln (1.60 \times 10^{-5}\ s^{-1}) + 5.985$$

$$= 1.60 \times 10^{-5}\ s^{-1} \times e^{5.985} = 6.36 \times 10^{-3}\ s^{-1}.$$

Arrhenius Eq. (6.40) is purely an empirical equation that gives a reasonably good representation of temperature dependence of the rate constant. An elementary account of two common theories of reaction rates leading to Arrhenius equation, viz. collision theory and transition state theory are given below.

Collision Theory

One of the simplest way to derive Arrhenius equation is to perceive that reactions take place by collision between the reactant molecules. If we assume that the rate of reaction is equal to the rate of collisions per unit volume per unit time multiplied by the fraction of collisions that have sufficient relative kinetic energy to

surmount the energy barrier, ε^* (per colliding pair of molecules), then it can be shown using kinetic theory of gases (about which you will study in higher classes) that the rate constant is given by the expression:

$$k = Z_{AB}\, e^{-\varepsilon^*/kT} \quad (6.45)$$

Here Z_{AB} is the collision frequency factor (the number of collisions between reactant molecules A and B per unit volume per unit time divided by the N_A and N_B, the number of molecules per unit volume of A and B respectively). It can be shown by kinetic theory of gases that,

$$Z_{AB} = (8\, k\, T/\pi\, \mu)^{1/2}\, \pi\, d^2 \quad (6.46)$$

Here $\mu = m_A\, m_B/\, (m_A + m_B)$ is the reduced mass of the colliding molecules, m_A and m_B are the individual masses of the moecules A and B respectively and $d = r_A + r_B$, is the sum of the radii of two reactant molecules. Thus, we have:

$$k = (8\, k\, T/\pi\, \mu)^{1/2}\, \pi\, d^2\, e^{-\varepsilon^*/kT} \quad (6.47)$$

If we assume that energy required for Avogadro number of effective collisions is $E_a = N_A\varepsilon^*$, then

$$k = (8kT/\pi\, \mu)^{1/2}\, \pi\, d^2\, e^{-E_a/RT} \quad (6.48)$$

The physical meaning of the activation energy is the minimum relative kinetic energy the reactant molecules must possess for conversion into the product molecules during their collision. This means that the fraction of successful collision is equal to the Boltzmann factor $e^{-E_a/RT}$, while the pre-exponential factor corresponds to collision frequency as depicted above whatever may be the energy of the colliding molecules. However, besides the requirement of energy, the molecules must be oriented properly in space for a collision to be successful. We can illustrate (Fig. 6.6) the importance of the orientation factor in space for the reaction:

$$NO_2(g) + NO_2(g) \rightarrow N_2O_4\,(g)$$

Thus if Z_{AB} is the collision frequency, P is the orientation factor also called steric factor then

$$k = P\, Z_{AB}\, e^{-E_a/RT} \quad (6.49)$$

Comparing Eq. (6.49) with Eq. (6.42), we note that $A = P\, Z_{AB}$.

Transition State Theory

According to this theory, the reactant molecules must come together to form an activated complex, whose energy is higher than the reactant molecules before the reactnts are converted into product molecules. The activated complex is supposed to be in equilibrium with the reactant molecules and it has all the attributes of a normal molecule except that one of the vibrational degrees of freedom is converted into translational degree of freedom along the reaction coordinate. The potential energy of the interacting molecules during collision depends upon the relative position of the nuclei of various atoms. The dependence of potential energy upon the coordinates of nuclei for any reaction system can be represented by a potential energy surface (Fig. 6.7a, b & c). Within the potential energy, there is a minimum energy pathway between reactants and products and is called the reaction pathway or reaction coordinate. Along the reaction coordinate there is

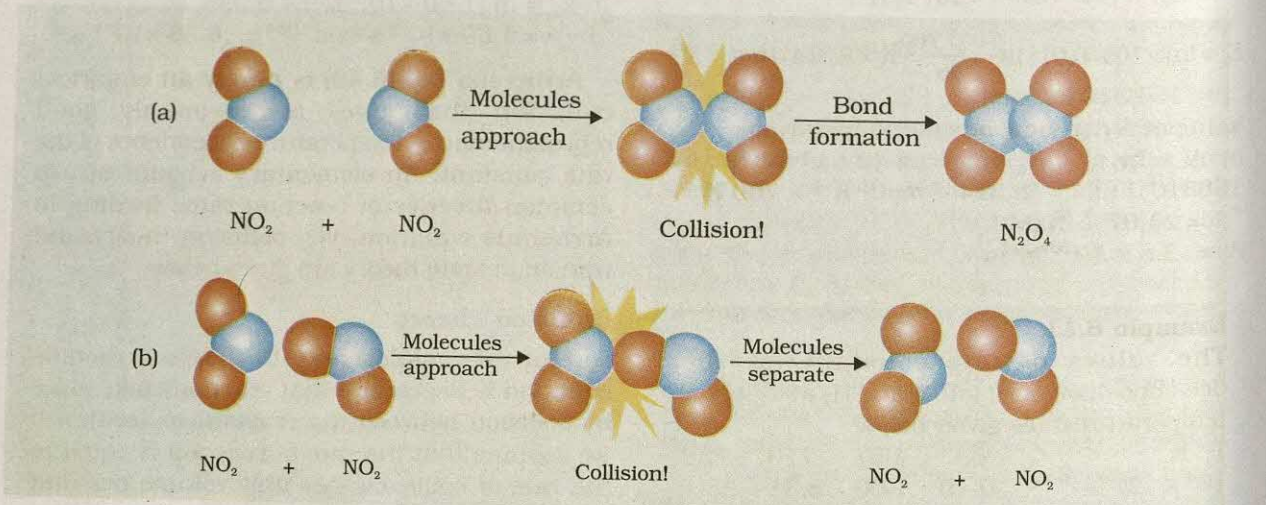


Fig. 6.6 *Orientation of colliding NO_2 molecules is proper in (a) but 'not' in (b) for the reaction to take place.*

simultaneous movement of various nuclei to give the product molecules. **Transition state** (its existence has been shown experimentally by Ahmed H. Zewail) is the configuration of atoms in the activated complex, which, if attained leads to the formation of the products with a frequency equal to k_bT/h. Here k_b is Boltzmann constant, T is the temperature of the reaction and h is Planck constant. If K^* is the equilibrium constant and Δ_rG^* (called Gibbs energy of activation = $\Delta_rH^* - T\Delta_rS^*$)is the corresponding Gibbs energy change when an activated complex is formed from the reactants, then the rate constant is given by the equation:

$$k = (k_bT/h)K^* = (k_bT/h)e^{\Delta_rS^*/R}\ e^{-\Delta_rH^*/RT} \quad (6.50)$$

Comparing with Eq. (6.42) we can say that $E_a = \Delta_rH^*$ and $A = (k_bT/h)\ e^{\Delta_rS^*/R}$. Sometimes right hand side of, 6.50 is multiplied by a correction factor, κ (transmission coefficient), and the equation becomes

$$k = \kappa\,(k_bT/h)K^* = \kappa\,(k_bT/h)e^{\Delta_rS^*/R}\ e^{-\Delta_rH^*/RT}$$

For an elementary reaction, the ratio of the rate constant, k_f, for the forward reaction and the rate constant, k_r, for the reverse reaction is equal to the equilibrium constant for the reaction i.e., $K = k_f / k_r$, and the activation energy, E_a^f, of the forward reaction and the activation energy, E_a^r of the reverse reactions are related to the enthalpy of the reaction by the equation:

$$\Delta_rH^\ominus = E_a^f - E_a^r$$

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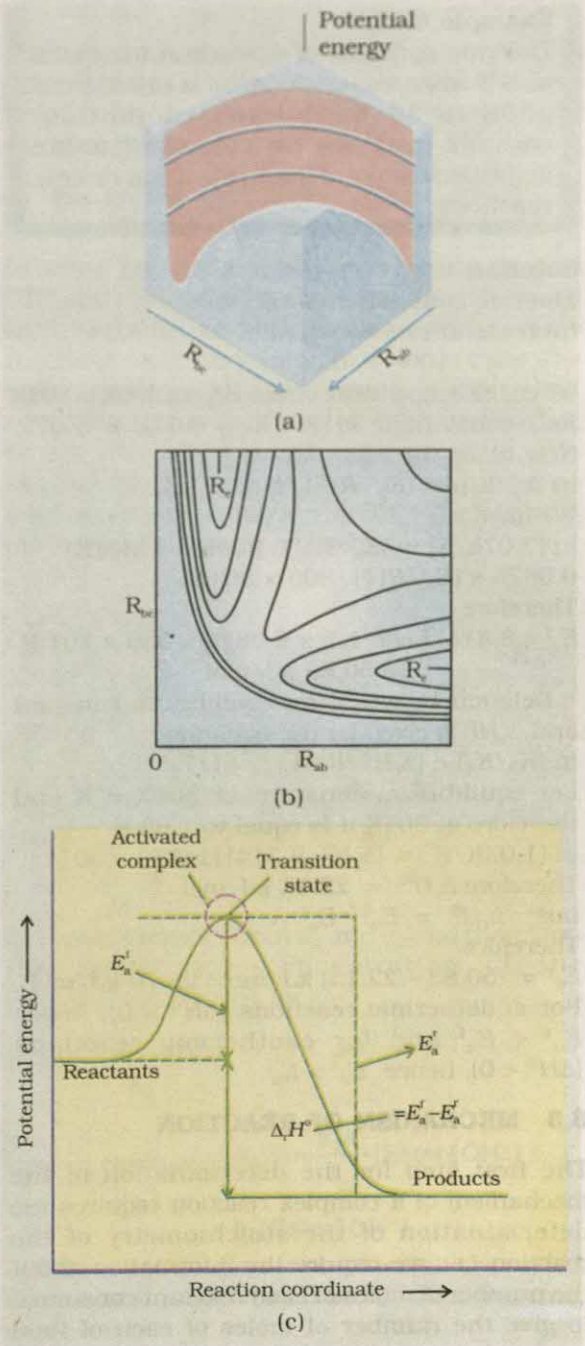


Fig. 6.7 *(a) The Potential energy surface for the reaction $H_a+H_bH_c \rightarrow H_aH_b+H_c$. R_{ab} and R_{bc} represent the distances between the corresponding hydrogen atoms.*
(b) The contour diagram showing contours of equal potential energy corresponding to potential energy surface (6.7a).
(c) Potential energy diagram for a reaction along a reaction coordinate.

Example 6.13
The rate constant of a reaction increases by 7% when its temperature is raised from 300K to 301K while its equilibrium constant increases by 3%. Calculate the activation energy of the forward and reverse reactions.

Solution
The rate constant at 300K = k
Increase in rate constant
= k × 7/100 = 0.07k
When the temperature is raised from 300K to 301K
Rate constant at 301K = k + 0.07k = 1.07k
Now using the equation
$\ln [k_2/k_1] = [E_a^f/R][1/T_1 - 1/T_2]$
We have
$\ln [1.07k/k] = [E_a^f/R][1/300K - 1/301K]$
$0.0676 = [E_a^f/R][1/300 \times 301K]$
Therefore
$E_a^f = 8.314\ Jmol^{-1}K^{-1} \times 0.0676 \times 300 \times 301\ K$
$= 50.83\ kJ/mol$

Relation between the equilibrium constant and $\Delta_r H^\ominus$ is given by the equation:
$\ln [K_2/K_1] = [\Delta_r H^\ominus/R][1/T_1 - 1/T_2]$
Let equilibrium constant at 300K = K and therefore at 301K it is equal to 1.03 K
$\ln (1.03K/K) = [\Delta_r H^\ominus/8.314][1/300 \times 301]$
Therefore $\Delta_r H^\ominus = 22.13$ kJ/mol
but $\Delta_r H^\ominus = E_a^f - E_a^r$
Therefore
$E_a^r = (50.83 - 22.13)$ kJ/mol$= 28.70$ kJ/mol
For endothermic reactions ($\Delta H^\ominus > 0$), hence $E_a^r < E_a^f$ and for exothermic reactions ($\Delta H^\ominus < 0$), hence $E_a^r > E_a^f$.

6.3 MECHANISM OF REACTION

The first step for the determination of the mechanism of a complex reaction requires the determination of the stoichiometry of the reaction i.e., we require the information about the number of moles of each reactant consumed to give the number of moles of each of final products. In some reactions, intermediates are produced which accumulate during the early period of the reaction, reach to a maximum concentration and then react to give the final products. The determination of the mechanism of a reaction is not an easy task and requires the experience and ingenuity of the scientist. The necessary condition for a mechanism to fulfil is that it must lead to the correct rate law. However, this does not guarantee that the mechanism is true. The kinetic study has to be supplemented by various techniques to verify the desirability of including certain elementary steps in the reaction mechanism. We shall now describe the mechanism of some simple reactions.

1. Reaction involving two first order consecutive steps.

In such reactions, a reaction takes place in two steps both of which are first order.

$R \xrightarrow{k_1} I$ I
$I \xrightarrow{k_2} P$ II

Now I is produced by step I and consumed by step II. The intermediate I accumulates and reaches a maximum after which it decays to zero concentration and is converted into the final product as shown in Fig. 6.8.

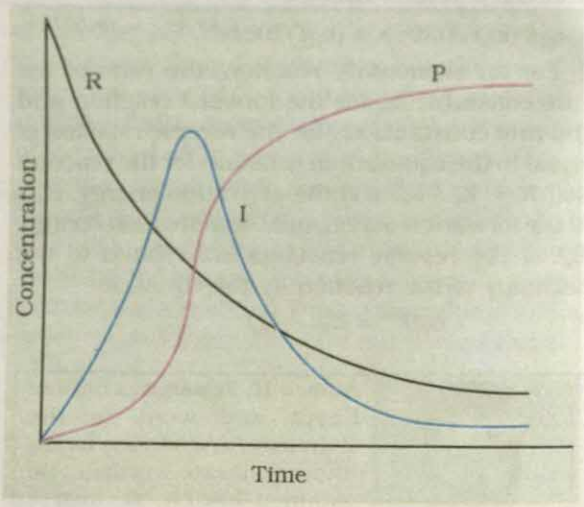


Fig. 6.8 *Concentration profiles of R(reactants). I(intermediate)and P(Product) as a function of time.*

2. Reactions involving slow step

If a reaction takes place by a sequence of steps and one of the steps is slow, then the rate determining step is the slow step. The rate of this step may be slow either due to low value of the rate constant or a very low concentration of one or more of the reacting species in that elementary reaction. For example, in the reaction

$R \xrightarrow{k_1} I$
$I \xrightarrow{k_2} P$

if $k_1 << k_2$ then I is converted into the product as soon as it is formed and we can say

$$\frac{-d[R]}{dt} = \frac{d[P]}{dt} = k_1[R]$$

This can be understood easily by the following analogy. Suppose a message is to be sent from New York to New Delhi. In the first case, a person writes a letter and sends it by post and then the postman delivers this letter to the second person. The two steps can be written as:

Message with sender $\xrightarrow{\text{By Post}}$ Message in New Delhi

Message with postman $\xrightarrow{\text{Delivery Time}}$ Message with receiver

It is obvious that the first step is so slow that nearly all the time is taken by it and hence rate determining. In the second case, the sender in New York sends the message by telegram which is then delivered by the postman in New Delhi. We can now write the two steps:

Message with sender $\xrightarrow{\text{Telegram}}$ Message in New Delhi

Message with postman $\xrightarrow{\text{Delivery Time}}$ Message with receiver

In this case, the first step is very fast and takes only a few seconds and the rate determining step is the time taken by the postman to deliver the message.

In the reaction,

$$3ClO^- \rightarrow ClO_3^- + 2Cl^-$$

various steps are:

$$ClO^- + ClO^- \rightarrow ClO_2^- + Cl^- \text{ slow step}$$

(rate determining step)

$$ClO_2^- + ClO^- \rightarrow ClO_3^- + Cl^- \text{ fast step}$$

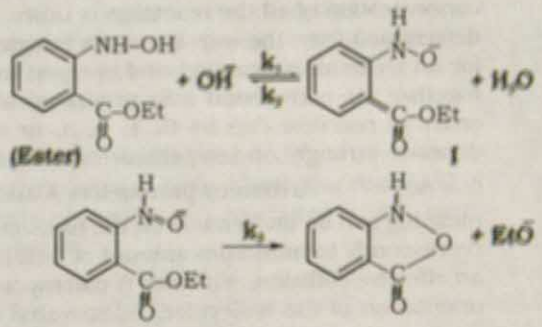
$\therefore$ rate $= k_1[ClO^-]^2$

3. Reactions for which Steady state hypothesis is valid

A reaction may take place in a number of steps and may have several intermediates. In the steady state hypothesis, we assume that the intermediates are so reactive that after a brief initial period (called induction period) their concentrations rise from zero to a small value and remain constant for most of the duration of the reaction i.e., we can assume that change in the concentration with time for these reactive intermediates is zero. This assumption is very helpful for deriving the rate expression for complex reactions.

4. Reactions involving Intermediates in Equilibrium with the Reactants

In some reactions specially involving H^+ and OH^-, there is an equilibrium established between the reactants as both forward and reverse reactions have very large rate constants. The intermediate thus formed reacts so slowly that equilibrium concentration of the intermediate is not disturbed much. For example, the displacement of $C_2H_5O^-$ from o-hydroxyamino ethyl benzoate is catalysed by OH^-. The following mechanism has been suggested :



k_3 is much smaller than k_1 and k_2 and therefore, the equilibrium concentration of the intermediate is given by

$$[I] = \frac{k_1[Ester][OH^-]}{k_2}$$

$$\text{Rate of reaction} = k_3[I] = \frac{k_3 k_1}{k_2}[Ester][OH^-]$$

$$= k_0[Ester][OH^-]$$

This is a second order reaction but the overall rate constant involves all the 3 rate constants, or we have

$$k_0 = \frac{k_3 k_1}{k_2}$$

Here k_0 is called the overall rate constant of the reaction and depends on the values of rate constants k_1, k_2 and k_3.

SUMMARY

The rate of a reaction is related to the rate of decrease of concentration of the reactant or the rate of increase of concentration of the product. For the sake of consistency rate is defined by:

$$\text{Rate} = -\frac{1}{\upsilon_R}\frac{d[R]}{dt} = \frac{1}{\upsilon_P}\frac{d[P]}{dt}$$

Here, [R] and [P] are the concentration of the reactant and product respectively and υ_R and υ_P are the corresponding stoichiometric coefficients in the chemical equation for the reaction. The rate of reaction depends upon a number of factors such as concentration of reactants, products, temperature of the reaction and presence of the catalyst and light etc. Elementary reaction takes place in a single step whereas, a complex reaction takes place in a number of steps. The rate law gives a mathematical relation between rate and the concentration of reactants, products and even some foreign substances. The rate law has to be determined experimentally and cannot be predicted. **Order of reaction with respect to a reactant is the power of its concentration to which the rate of reaction is directly proportional. Sum of all such powers of concentration for different reactants gives the overall order of reaction.** Rate constant is the rate of reaction when concentration of all the reactants is unity. Rate constant and the order of reaction can be determined from the rate law or its integrated rate equation. Molecularity is defined only for an elementary reaction and is equal to the number of molecules which should come together for conversion into products. Molecularity is limited to 1, 2 or 3, whereas, order of reaction can be 0, 1, 2, 3, or even a fractional number. The rate constant depends strongly on temperature and is represented adequately by Arrhenius equation ($k = Ae^{-E_a/RT}$). Arrhenius parameters A and E_a are important quantities and their physical meaning can be understood on the basis of theories of reaction rate. In collision theory, E_a corresponds to minimum amount of relative kinetic energy of the colliding molecules for an effective collision, whereas, A corresponds to collisional frequency with suitable space orientation of the molecules. In activated complex theory, E_a corresponds to the energy difference between the activated complex and the reactant molecules. $A = k\frac{kT}{h}e^{\Delta_r S^*/R}$ where $\Delta_r S^*$ is the entropy difference between the activated complex and the reactant molecules. Mechanism of a complex reaction gives the sequence of steps which lead to the conversion of the reactants into products as represented by the chemical equation. The mechanism must lead to correct rate law.

EXERCISES

6.1 From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

(a) $3NO\,(g) \longrightarrow N_2O\,(g) + NO_2\,(g)$; Rate = $k\,[NO]^2$

(b) $H_2O_2\,(aq) + 3I^-\,(aq) + 2H^+ \longrightarrow 2H_2O\,(l) + I_3^-$; Rate = $k[H_2O_2]\,[I^-]$

(c) $CH_3CHO\,(g) \longrightarrow CH_4\,(g) + CO\,(g)$; Rate = $k[CH_3CHO]^{3/2}$

(d) $CHCl_3\,(g) + Cl_2\,(g) \longrightarrow CCl_4\,(g) + HCl\,(g)$; Rate = $k[CHCl_3][Cl_2]^{1/2}$

(e) $C_2H_5Cl\,(g) \longrightarrow C_2H_4\,(g) + HCl\,(g)$; Rate = $k[C_2H_5Cl]$

6.2 For the reaction:

$2A + B + C \longrightarrow A_2B + C$

the rate = $k[A][B]^2$ with $k = 2.0 \times 10^{-6}\ M^{-2}s^{-1}$. Calculate the initial rate of the reaction when [A] = 0.1M, [B] = 0.2M and [C] = 0.8M. If the rate of reverse reaction is negligible then calculate the rate of reaction after [A] is reduced to 0.06M.

6.3 The decomposition of NH_3 on platinum surface is zero order. What are the rate of production of N_2 and H_2 if k = 2.5×10^{-4} Ms^{-1}.

6.4 The decomposition of dimethyl ether leads to the formation of CH_4, H_2 and CO and the reaction rate is given by

Rate = $k[CH_3OCH_3]^{3/2}$

The rate of reaction is followed by increase in pressure in a closed vessel and the rate can also be expressed in terms of the partial pressure of dimethyl ether i.e.,

rate = $k(p_{CH_3OCH_3})^{3/2}$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

6.5 Mention the factors that affect the rate of a chemical reaction.

6.6 A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is

(i) doubled. (ii) reduced to 1/2?

6.7 What is the effect of temperature on the rate constant of reaction? How can this temperature effect on rate constant be represented quantitatively?

6.8 In a pseudo first order hydrolysis of ester in water the following results were obtained:

t/s	0	30	60	90
[Ester]/M	0.55	0.31	0.17	0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

6.9 A reaction is first order in A and second order in B.

(i) Write differential rate equation.

(ii) How is the rate affected when the concentration of B is tripled?

(iii) How is the rate affected when the concentration of both A and B is doubled?

6.10 In a reaction between A and B, the initial rate of reaction was measured for different initial concentrations of A and B as given below:

A/M	0.20	0.20	0.40
B/M	0.30	0.10	0.05
r_0/M s^{-1}	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

What is the order of reaction with respect to A and B?

6.11 Reaction between NO_2 and F_2 to give NO_2F takes place by the following mechanism:

$NO_2(g) + F_2(g) \xrightarrow{\text{slow}} NO_2F(g) + F(g)$

$NO_2(g) + F(g) \xrightarrow{\text{fast}} NO_2F(g)$

Write the rate expression for the reaction.

6.12 The following results have been obtained during the kinetic studies of the reaction:

$2A + B \longrightarrow C + D$

Experiment	[A]/M	[B]/M	Initial rate of formation of D/M min^{-1}
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

6.13 The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

Experiment	[A]/M	[B]/M	Initial Rate/M min^{-1}
I	0.1	0.1	2.0×10^{-2}
II	—	0.2	4.0×10^{-2}
III	0.4	0.4	—
IV	—	0.2	2.0×10^{-2}

6.14 Calculate the half life of a first order reaction from their rate constants given below:

(a) 200 s^{-1} (b) 2 min^{-1} (c) 4 $year^{-1}$

6.15 The experimental data for decomposition of N_2O_5 [$2N_2O_5 \longrightarrow 4NO_2 + O_2$] in gas phase at 318K are given below:

t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [N_2O_5]/M$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(a) Plot $[N_2O_5]$ against t
(b) Find the half life period for the reaction
(c) Draw a graph between $\log[N_2O_5]$ and t
(d) What is rate law
(e) Calculate the rate constant
(f) Calculate the half life period from k and compare it with (b).

6.16 The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its $1/16^{th}$ value?

6.17 The rates of most reactions double when their temperature is raised from 298K to 308K. Calculate their activation energy.

6.18 The rate constant for the decomposition of N_2O_5 at various temperatures is given below:

$T/^0C$	0	20	40	60	80
$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between ln k and $1/T$ and calculate the values of A and E_a. Predict the rate constant at 30^0 and 50^0C.

6.19 The half life for radioactive decay of ^{14}C is 5730 y. An archaelogical artefact contained wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

6.20 During nuclear explosion, one of the products is ^{90}Sr with half life of 28.1 y. If 1 μg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

UNIT 7

SURFACE CHEMISTRY

OBJECTIVES

After studying this Unit, you will be able to:

- describe interfacial phenomenon and its importance.
- define adsorption and classify it into physical and chemical adsorption.
- learn about factors controlling adsorption from gases and solutions on solids.
- correlate adsorption results on the basis of Freundlich and Langmuir adsorption isotherms.
- understand the nature of the colloidal state, and learn the preparation and properties of various types of colloids.
- learn about emulsions, their types, preparation and properties.
- learn about the uses of colloids.
- appreciate the role of catalysts in industrial processes.

"Some of the most important chemicals are produced industrially by means of reactions that occur on the surfaces of solid catalysts."

Surface chemistry is the chemistry at the boundary separating two bulk phases. This boundary which is also known as *surface* or *interface* is represented by separating the bulk phases by a hyphen or a slash. For example, the interface between a solid and liquid may be represented by solid-liquid or solid/liquid interface. There is no interface between gases due to their complete miscibility. The bulk phases may be pure compounds or solutions. The interface is usually a few molecules thick but its area depends on the size of the particles of the bulk phases. Dissolution and crystallization electrode processes, heterogeneous catalyses, corrosion and many other important phenomena take place at interfaces. Therefore, the subject of surface chemistry is of great importance not only from the academic point of view but also from the point of view of its important applications in industry, analytical chemistry and our daily lives.

To carry out surface studies, it is necessary to have a really clean surface. It is now possible to obtain ultra clean surfaces of metals by heating them under very high vacuum (10^{-8} to 10^{-9} pascal). Such clean solid materials have to be stored in vacuum, otherwise their surface will be covered by molecules of oxygen and nitrogen from air.

In this Unit we shall be studying some important features of surface chemistry such as adsorption, catalysis, colloids, emulsions and micelles.

7.1 ADSORPTION

In the interior of a liquid or a solid, molecules experience attraction on all sides, whereas

molecules on the surface have other neighbouring molecules only below and on the sides. As a result molecules at the surface experience a net attraction downward and move toward the interior to increase attractions. The molecules on the surface, therefore, have higher energy than those inside (Fig. 7.1). The result is that the surface of a solid or a liquid is in a state of strain or tension on account of the unbalanced or residual forces.

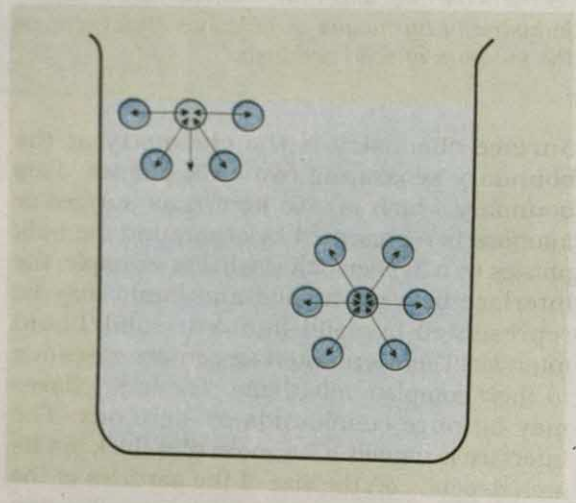


Fig. 7.1 Molecules at the surface of a liquid experience a net attraction downward.

The surface of a solid (or a liquid), therefore, tends to attract and retain other molecules when it is brought in contact with a gas or a solution. For example, when a finely divided active carbon or clay is stirred into a dilute solution of a dye, we observe that the intensity of colour in the solution is decreased. Similarly, when a finely divided solid is exposed to a gas at low pressure, the pressure decreases noticeably. In both these situations, the dye or the gas are adsorbed on the solid surface.

As these molecules remain only at the surface and do not go deeper into the bulk, their concentration is more at the surface than in the bulk of the solid or liquid as the case may be. **This phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting into a higher concentration of the molecules on the surface is called adsorption**. *As a result of adsorption, there is a decrease of surface energy.* The substance on the surface of which adsorption takes place is called **adsorbent** and the substance adsorbed is known as **adsorbate**. **The process of removal of an adsorbed substance from the surface on which it is adsorbed is called desorption**. It is the reverse of adsorption and can be brought about by heating or by reducing the pressure.

Solids, particularly when finely divided, have a large surface area and, therefore, show this property of adsorption to a much larger extent. Charcoal, silica gel, alumina gel, clay etc. are very good adsorbents because they have highly porous[1] structures and hence large surface areas. Colloids, as you shall study later in this Unit, on account of their extremely small dimensions, possess enormous surface area per unit mass and are, therefore, also good adsorbents.

7.1.1 Difference between Adsorption and Absorption

Adsorption is quiet different from absorption. **In absorption, the molecules of a substance are uniformly distributed throughout the body of a solid or a liquid**, whereas in adsorption, the molecules of a substance are present in higher concentration at the surface of the adsorbent. *Absorption of a substance A by a substance B means that A is uniformly distributed all over B. Adsorption on the other hand, means that A is present on the surface of B, and the concentration of A in parts of B away from the surface is negligible.*

Water vapours, for example, are absorbed by anhydrous calcium chloride while these are adsorbed by silica gel. It may be noted that in certain cases, adsorption and absorption both take place simultaneously and are indistinguishable. In such cases, the word **sorption** is used to describe the phenomenon.

7.1.2 Physisorption and Chemisorption

Adsorption can be classified into **Physisorption** and **Chemisorption**. In physisorption (short name for physical adsorption), the adsorbate is held on the surface by weak van der Waals attraction while in chemisorption, (short name for chemical adsorption) the binding is of

[1] *When adsorbents are porous, the adsorbate may actually condense in the pores. This process is called capillary condensation.*

chemical nature i.e., the molecules/atoms of adsorbate form chemical bonds with the adsorbent surface. *The physisorption displays the features of a physical process, such as condensation, whereas chemisorption shows the features of a chemical reaction.*

Adsorption generally occurs with release of energy i.e., it is **exothermic** in nature. A spontaneous process requires a negative ΔG. Since the translational freedom of the adsorbate is reduced when it is adsorbed, ΔS is generally negative. Therefore, in order for $\Delta G = \Delta H - T\Delta S$ to be negative, ΔH must be negative and hence the process is exothermic[2]. In an adsorption process, the enthalpy change for the adsorption of one mole of an adsorbate on an adsorbent surface is called the **Enthalpy of Adsorption**. The enthalpy of chemisorption is of the order of 200 kJ mol^{-1} while for physical adsorption it is of the order of 20 kJ mol^{-1}. The comparison of the two types of adsorption is given in Table 7.1.

Table 7.1 Comparison between Physisorption and Chemisorption

Physisorption	Chemisorption
1. Enthalpy of adsorption, usually is of the order of –20 kJ mol^{-1}.	Enthalpy of adsorption, is of the order of –200 kJ mol^{-1}.
2. Molecules of adsorbate and adsorbent are held by van der Waals interactions.	Molecules of adsorbate and adsorbent are held by chemical bonds.
3. It usually takes place at low temperature and decreases with increasing temperature.	It takes place at relatively high temperatures.
4. It is not very specific i.e. all gases are adsorbed on all solids to some extent.	It is highly specific and takes place when there is some possibility of compound formation between the adsorbate and the adsorbent molecules.
5. Multi-molecular layers may be formed on the adsorbent	Usually mono-molecular layer is formed on the adsorbent.

Adsorption of Nitrogen on Iron

The difference between physisorption and chemisorption is typified by the behaviour of nitrogen on iron. At 83K nitrogen is physisorbed on iron surface as nitrogen molecules, N_2. The amount of nitrogen adsorbed decreases rapidly as the temperature rises. At room temperature, practically there is no adsorption of nitrogen on iron. At 773K and above, nitrogen is chemisorbed on the iron surface as nitrogen atoms.

7.2 ADSORPTION OF GASES ON SOLIDS

Almost all solids adsorb gases to some extent. If we expose activated charcoal (say, in a gas mask) to chlorine gas, charcoal adsorbs chlorine. Moisture in air, though present to a small extent, is strongly adsorbed over silica gel. Silica gel is, therefore, used for drying air by adsorption of moisture. Charcoal also adsorbs polluting gases present in air in small concentration. Gases such as H_2, O_2, N_2 and CO are adsorbed by transition metals e.g. nickel and cobalt.

7.2.1 Factors affecting Adsorption of Gases on Solids

The extent of adsorption of a gas on a solid adsorbent depends upon the following factors:
(a) Nature of the adsorbate (b) Nature of the adsorbent (c) Specific area of the adsorbent (d) Pressure of the gas (e) Temperature (f) Activation of adsorbent.

We shall now discuss the role of these factors:

(a) Nature of the adsorbate: Physical adsorption is nonspecific in nature and, therefore, every gas gets adsorbed on the surface of any solid to a lesser or greater extent. However, under given conditions of temperature and pressure, the easily liquefiable gases like NH_3, HCl, CO_2, etc. are adsorbed to a greater extent than the permanent gases such as H_2, O_2, N_2, etc. The ease with which a gas can be liquefied is primarily determined by its critical temperature, T_c which is the minimum temperature above which a gas cannot be liquefied howsoever high the pressure may be applied. It, therefore, means that the

[2] *In exceptional cases, chemisorption may be endothermic. For example, H_2 adsorbs endothermically on glass. In this case, the ΔS in the process $H_2(g) \rightarrow 2H(glass)$ is sufficiently positive to overcome the small positive enthalpy change. Similarly, highly hydrated solutes, when adsorbed on solids have positive ΔH but are accompanied by large positive ΔS due to release of water molecules on adsorption.*

higher the critical temperature, T_c of a gas, the more easily it will be liquefied and, therefore, more readily it will be adsorbed on the solid. Thus, 1 g of activated charcoal adsorbs 380 mL of sulphur dioxide (critical temperature 430K), 16 mL of methane (critical temperature 190K) and 4.5 mL of hydrogen (critical temperature 33K). Volumes of the gases reduced to 273K and 1 atm pressure.

In contrast to physical adsorption, the process of chemisorption is highly specific in nature and in this case, therefore, a gas gets adsorbed on the solid only if it enters into chemical combination with it.

(b) Nature of the adsorbent: Most common adsorbents are activated carbon, metal oxides (silica gel and aluminium oxide) and clay. Each of these have their characteristic adsorption properties.

(c) Specific area of the adsorbent: Specific area of an adsorbent is the surface area available for adsorption per gram of the adsorbent. The greater the specific area of the solid, the greater would be its adsorbing capacity. That is why porous or finely divided forms of adsorbents adsorb larger quantities of adsorbate. However, the pores should be large enough to allow the gas molecules to enter them.

(d) Pressure of the gas: Adsorption isotherms The extent of the adsorption of a gas on a solid is generally expressed as x/m where m is the mass of the adsorbent and x is the number of moles of the adsorbate when dynamic equilibrium has been attained between the free gas and the adsorbed gas. One can measure experimentally the relation between x/m and pressure (p) of the gas at a constant temperature. A relation or a graph between x/m and the pressure p of the gas at a constant temperature is called **adsorption isotherm**. Adsorption isotherms of different shapes have been experimentally observed. To account for these isotherms, many different adsorption isotherms have been proposed. Here we shall confine ourselves only to the Freundlich and Langmuir adsorption isotherms.

Freundlich Adsorption isotherms: In the case of adsorption of gases on solids, the relation between x/m and the pressure p of the gas at constant temperature is given by the equation:

$$\frac{x}{m} = k\,p^{1/n} \quad (n>1) \qquad (7.1)$$

where k and n are parameters of the equation depending upon the nature of the gas and the solid. According to this, x/m increases with increase of p but since n>1, therefore, x/m does not increase as rapidly as p as is evident from the isotherm (Fig. 7.2).

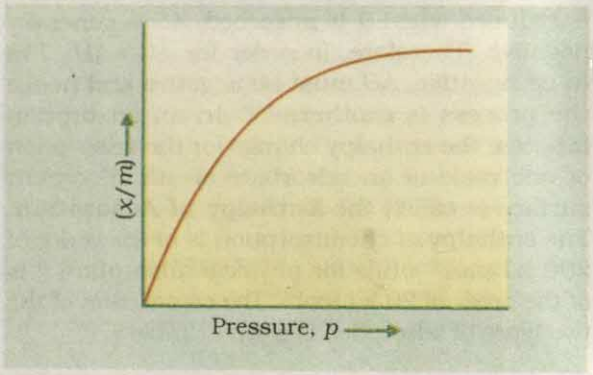


Fig. 7.2 *Freundlich adsorption isotherm.*

Taking logarithms on both sides of Eq. (7.1), we get

$$\log\frac{x}{m} = \log\,k + \frac{1}{n}\log\,p \qquad (7.2)$$

Thus, if we plot a graph between log (x/m) and log p, a straight line is obained. The slope of the line (Fig. 7.3) is equal to 1/n and the intercept on log (x/m) axis will correspond to log k. Therefore, from this graph it is possible to find out value of k and n. Experimental results conform to Freundlich adsorption isotherm if a plot of log(x/m) vs log p yields a straight line.

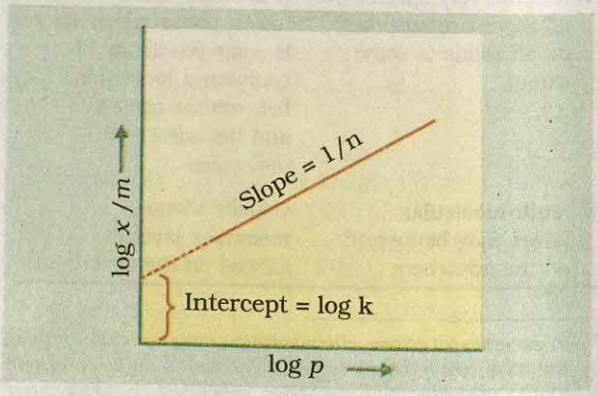


Fig. 7.3 *Graph of log x/m vs log p.*

Langmuir Adsorption isotherm: One of the drawbacks of the Freundlich adsorption isotherm is that it fails at high pressure of the gas. Langmuir derived an adsorption isotherm on theoretical considerations based on kinetic theory of gases. This is named as the *Langmuir adsorption isotherm*. This isotherm is based on the assumption that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not nearby sites are occupied. In his derivation, Langmuir considered adsorption to consist of the following two opposing processes:

(i) Adsorption of the gas molecules on the surface of the solid.

(ii) Desorption of the adsorbed molecules from the surface of the solid.

Langmuir believed that eventually a dynamic equilibrium is established between the above two opposing processes. He also assumed that the layer of the adsorbed gas was only one molecule thick i.e., unimolecular. Since such type of adsorption is obtained in the case of **chemisorption**, Langmuir adsorption isotherm works particularly well for chemisorption.

The Langmuir adsorption isotherm is represented by the relation

$$\frac{x}{m} = \frac{a\,p}{1 + b\,p} \qquad (7.3)$$

where a and b are two Langmuir parameters. At very high pressure, the above isotherm acquires the limiting form.

$$\frac{x}{m} = \frac{a}{b} \text{ (at very high pressure)} \qquad (7.4a)$$

At very low pressure, Eq. (7.3) is reduced to

$$x/m = a\,p \text{ (at very low pressure)} \qquad (7.4b)$$

In order to determine the parameters a and b, Eq. (7.3) may be written in its inverse form:

$$\frac{m}{x} = \frac{1 + b\,p}{a\,p} = \frac{b}{a} + \frac{1}{ap} \qquad (7.5)$$

A plot of m/x against $1/p$ gives a straight line with slope and intercept equal to 1/a and b/a, respectively. Thus, both parameters can be determined.

The Langmuir isotherm, in the form of Eq. (7.3) is generally more successful in interpreting the data than the Freundlich isotherm when a monolayer is formed. A plot of x/m versus p is shown in (Fig. 7.4). At low pressures, according to Eq. [7.4 (b)], pressure x/m increases linearly with p. At high pressure according to Eq. [7.4 (a)], x/m becomes constant i.e. the surface is fully covered and change in pressure has no effect and no further adsorption takes place, as is evident from Fig. 7.4.

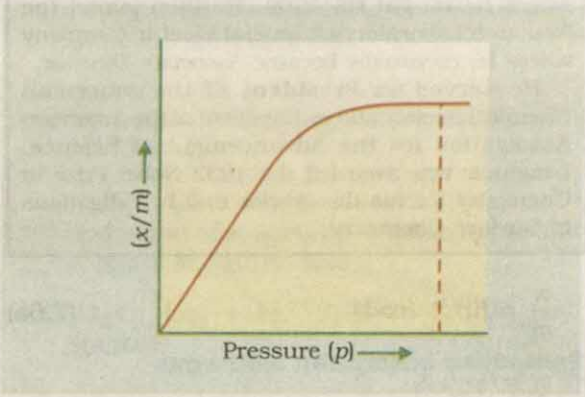


Fig. 7.4 *Langmuir Adsorption isotherm.*

(e) Effect of temperature: Adsorption isobar
Adsorption is generally temperature dependent. Mostly adsorption processes are exothermic and, therefore, adsorption decreases with increasing temperature. However, as expected for endothermic adsorption processes, adsorption increases with increase in temperature.

7.3 ADSORPTION FROM SOLUTIONS

Solids can adsorb dissolved substances from solutions also. Common examples are the adsorption of colour impurities by activated carbon in decolourising of solutions. The chromatographic separation is possible due to different adsorption tendencies of the solutes of a solution. Many inorganic precipitates also act as adsorbents.

Freundlich adsorption and Langmuir adsorption isotherms have been found to be applicable in the adsorptions from solutions. Temperature dependence here also is similar to that for adsorption of gases. However, in place of equilibrium pressures, we use equilibrium concentrations of the adsorbates in the solution and the isotherms take the form

Irving Langmuir
(1881-1957)

Irving Langmuir (1881-1957) did postgraduate work in Physical Chemistry under Nernst in Gottingen which earned him the degrees of M.A. and Ph.D. in 1906. Langmuir joined as Instructor in Chemistry at Stevens Institute of Technology, Hoboken, New Jersey where he taught till 1909. He then joined the Research Laboratory of General Electric Company where he eventually became Associate Director.

He served as President of the American Chemical Society and as President of the American Association for the Advancement of Science. Langmuir was awarded the 1932 Nobel Prize in Chemistry for his discoveries and investigations in Surface Chemistry.

$$\frac{x}{m} = Kc^{1/n} \quad (n>1) \qquad (7.6a)$$

Freundlich adsorption isotherms

$$\frac{x}{m} = ac/(1+ bc) \qquad (7.6b)$$

Langmuir adsorption isotherms

The parameters of Eqs. (7.6a and 7.6 b) can be determined by the methods described earlier for adsorption of gases on solids.

7.4 CATALYSIS

A **catalyst** is *a substance that increases the rate of reaction without being consumed in the reaction.* The phenomenon of increase in the rate of a reaction with the help of a catalyst is known as **catalysis**. Since catalysts are not consumed in the reaction, very small, non-stoichiometric quantities are generally all that are required. Catalysts are employed in a number of industrial processes (Table 7.2). Nature is the master designer and user of catalysts. Even the simplest bacterium employs thousands of biological catalysts, known as enzymes, to speed up its cellular reactions. Every organism relies on enzymes to sustain life.

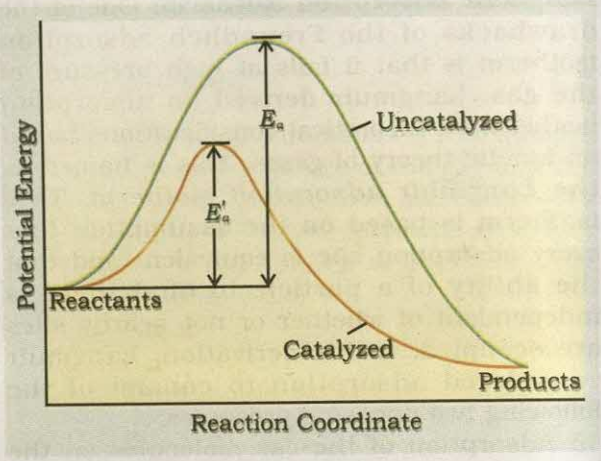


Fig. 7.5 *Comparison of the activation energies of a catalyzed and an uncatalyzed reaction.*

Each catalyst has its own specific way of functioning but in general, *a catalyst functions by lowering the energy of activation which in turn makes the rate constant larger and hence the rate of the reaction higher.*

Two important points stand out in Fig. 7.5.

(a) A catalyst speeds up the forward and reverse reactions to the same extent and therefore, does not affect the equilibrium constant.

(b) A catalyst lowers the energy of activation by providing a different mechanism for the reaction.

Table 7.2 Some Modern Processes Based on Catalysis

Reactants	Catalyst	Product
Homogeneous		
Propylene, oxygen	Mo(VI) complexes	Propylene oxide
Methanol, CO	$[Rh(CO)_2I_2]^-$	Acetic acid
Butadiene, HCN	Ni/Pd compounds	Adiponitrile
α-Olefin, CO, H_2	Rh/Pd compounds	Aldehydes
Heterogeneous		
Ethylene, O_2	Silver, caesium chloride on alumina	Ethylene oxide
Propylene, NH_3, O_2	Bismuth molybdates	Acrylonitrile
Ethylene	Organochromium and titanium	High-density polyethylene

7.4.1 Types of Catalysis

There are two broad categories of catalysis–*homogeneous* and *heterogeneous* depending on whether the catalyst is in the same phase as the reaction mixture or not.

1. Homogeneous Catalysis: *If the catalyst is present in the same phase as the reactants, it is called a homogeneous catalyst and this type of catalysis is called homogeneous catalysis.* It is believed that in homogeneous catalysis, a catalyst enters into chemical combination with one or more of the reactants forming an intermediate compound which then decomposes or combines with one of the reactants to produce the product and the catalyst is regenerated.

Table 7.2 shows industrial processes that employ these catalysts.

A thoroughly studied example of homogeneous catalysis is the hydrolysis of an organic ester (RCOOR').

$$R\text{–}\overset{\overset{\ddot{O}:}{\|}}{C}\text{–}\ddot{O}\text{–}R'(l) + H_2O(l) \overset{H^+(aq)}{\rightleftharpoons} R\text{–}\overset{\overset{\ddot{O}:}{\|}}{C}\text{–}\ddot{O}H(l) + R'\ddot{O}H(l)$$

Here R and R are alkyl groups, $R\text{–}\overset{\overset{\ddot{O}:}{\|}}{C}\text{–}\ddot{O}H$ is a carboxylic acid and $R'\text{–}\ddot{O}H$ is an alcohol. The reaction rate is low at room temperature but can be increased by adding a small amount of a strong inorganic acid which provides H^+ ion, that acts as a catalyst in the reaction.

Some other examples of homogeneous catalysts are:

(i) Catalytic decomposition of ozone by chlorine atoms in the gas phase.

$$O_3 + O \xrightarrow{Cl} 2O_2$$

(ii) Oxidation of CO by O_2 in the presence of NO as catalyst.

$$2CO\,(g) + O_2\,(g) \xrightarrow{NO} 2CO_2\,(g)$$

(iii) Hydrolysis of sugarcane solution in presence of dilute sulphuric acid.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}\,(aq)} + H_2O\,(l) \xrightarrow{H_2SO_4} \underset{\text{Glucose}}{C_6H_{12}O_6\,(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6\,(aq)}$$

CATALYTIC CONVERTER FOR AN AUTOMOBILE

The catalytic converter in the car's exhaust system which converts polluting exhaust gases into non-toxic ones contains a heterogeneous catalyst. In a single pass through the catalyst bed, CO and unburned petrol are oxidised to CO_2 and H_2O, while NO is reduced to N_2. Mixtures of transition metals and their oxides embedded in inert supports act as the catalyst.

$$2CO + O_2 \xrightarrow{\text{Catalyst}} 2CO_2$$

$$\underset{\text{(unburnt petrol)}}{\text{Hydrocarbons}} \xrightarrow[O_2]{\text{Catalyst}} CO_2 + H_2O$$

$$2NO \xrightarrow{\text{Catalyst}} N_2 + O_2$$

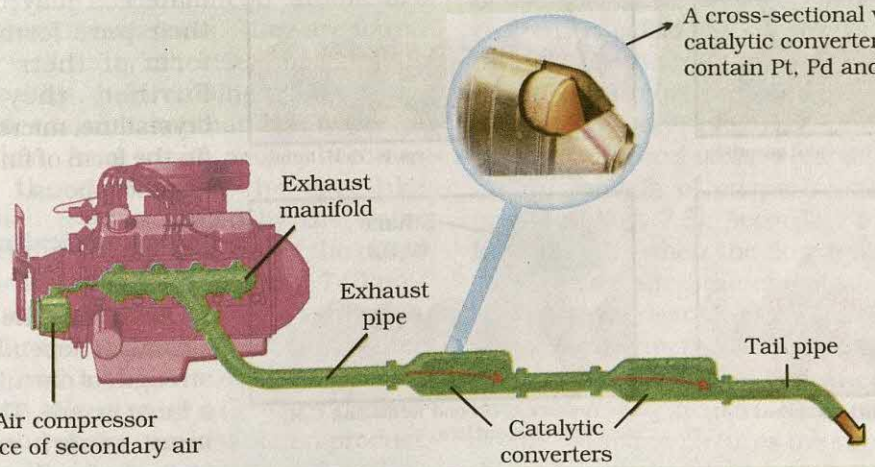


Fig.7.6 *A two-stage catalytic converter in an automobile.*

2. Heterogeneous Catalysis: In this type of catalysis the catalyst is present in a different phase than that of the reactants.

In heterogeneous catalysis, catalyst is generally a solid and the reactants are generally gases but sometimes liquid reactants are also used. It is also known as *surface catalysis* as the reaction starts at the surface of the solid catalyst. These catalysts have enormous surface areas between 1 to 500 m^2/g for contact. Interestingly, many reactions that occur on a metal surface such as the decomposition of HI on gold and the decomposition of N_2O on platinum, are zero order because the rate determining step occurs on the surface itself. Thus, despite an enormous surface area, once the reactant gas covers the surface, increasing the reactant concentration cannot increase the rate (Unit 5). Table 7.2 lists some industrial processes that employ heterogeneous catalysts.

One of the most important examples of heterogeneous catalysis is the addition of H_2 to the C=C bonds of organic compounds to form C-C bonds. The petroleum, plastics and food industries frequently use **catalytic hydrogenation**. The conversion of vegetable oil into margarine is one example.

The simplest hydrogenation process converts ethylene to ethane:

$$CH_2 = CH_2\,(g) + H_2\,(g) \longrightarrow CH_3 - CH_3\,(g)$$

In the absence of a catalyst, the reaction occurs very slowly. At high H_2 pressure in the presence of finely divided nickel, palladium or platinum, the reaction becomes rapid at ordinary temperatures. The catalyzed reaction is believed to take place through the following consecutive steps (Fig. 7.7):

(i) Chemical adsorption of reactants (C_2H_4, H_2) onto the surface of metals.

(ii) H_2 splits into H atoms which get chemically bound to the solid catalyst i.e. metal atoms (M)

$$H\text{-}H\,(g) + 2\,M\,(s) \rightleftharpoons 2\,M\text{-}H$$

(H atoms bound to metal surface)

This step is the rate-determining step in the overall process.

(iii) The H atoms migrate over the surface of the metal and eventually collide with an adsorbed C_2H_4 molecule and the reaction takes place.

$$C_2H_4\,(g) + 2\,M\text{-}H \rightleftharpoons C_2H_6\,(g) + 2\,M(s)$$

Some other examples of heterogeneous catalysis are:

(i) Manufacture of ammonia from N_2 and H_2 by Haber's process using iron as catalyst.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(ii) Synthesis of methyl alcohol (CH_3OH) from CO and H_2 using a mixture of copper, ZnO and Cr_2O_3 as catalyst.

$$CO(g) + 2H_2(g) \xrightarrow{Cu,\ ZnO\text{-}Cr_2O_3} CH_3OH(l)$$

7.4.2 Nature of Solid Catalysts

Solid catalysts may be metals, metal oxides, metal sulphides, clays etc. These materials may be used in their pure form or in the form of their mixtures. Further, they may be crystalline, microcrystalline (in the form of fine particles) or amorphous.

Important features of solid catalysts:

1. Activity: The activity of a catalyst depends upon the strength of chemisorption to a large extent. The reactant must adsorb reasonably strongly for the catalyst to be active but must not

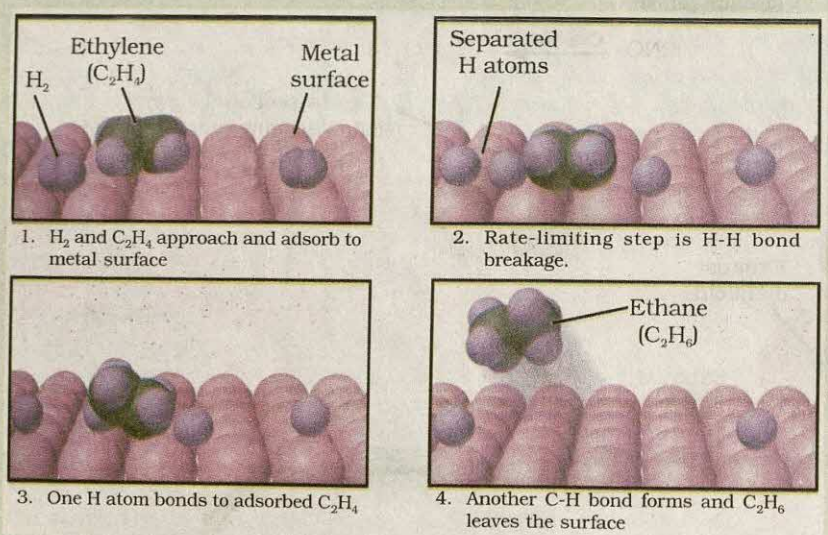


Fig. 7.7 *The metal catalyzed hydrogenation of ethylene.*

adsorb so strongly that they are immobilised and other reactants are left with no space on the catalyst surface for adsorption. It has been found that for hydrogenation the catalytic activity increases as we go from group 5 metals to group 11 with maximum activity shown by group 7-9 elements of the periodic table.

$$2H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(l)$$

2. Selectivity: The selectivity of a catalyst is its ability to direct a reaction to yield a particular product. For example, starting with H_2 and CO using different catalysts we get different products.

(i) $CO\ (g) + 3H_2\ (g) \xrightarrow{Ni} CH_4\ (g) + H_2O\ (g)$

(ii) $CO\ (g) + 2H_2\ (g) \xrightarrow{Cu/ZnO-Cr_2O_3} CH_3OH\ (g)$

(iii) $CO\ (g) + H_2\ (g) \xrightarrow{Cu} HCHO\ (g)$

Action of a catalyst is highly specific (selective) in nature i.e., a given substance can act as a catalyst only in a particular reaction and not for all the reactions. It means a substance which acts as a catalyst in one reaction may fail to catalyze other reaction i.e., a catalyst is highly selective in nature.

7.4.3 Shape-Selective Catalysis by Zeolites

The catalytic reaction that depends upon the porestructure of the catalyst and the size of the reactant and product molecules is called **shape–selective catalysis**. Zeolites are good shape–selective catalysts (Unit 8) because of their honeycomb-like structures. Zeolites are aluminosilicates i.e., three dimensional network silicates in which some silicon atoms are replaced by aluminium atoms. They are found in nature as well as synthesised for catalytic selectivity. Zeolites, before using as catalysts, are heated in vacuum so that the water of hydration is lost. As a result, zeolite becomes porous i.e., the cavities in the cage-like structure which were occupied by the water molecules become vacant. The size of the pores generally varies between 260 pm and 740 pm. Thus only those molecules can be adsorbed in these pores whose size is small enough to enter these cavities and also leave easily.

The reactions taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of the zeolites. That is why these types of reactions are called '**shape-selective catalysis**' reactions.

Zeolites are being very widely used as catalysts in **petrochemical industries** for cracking of hydrocarbons and isomerisation. An important zeolite catalyst used in the petroleum industry is ZSM-5. It converts alcohols directly into gasoline (petrol) by dehydrating them so that a mixture of hydrocarbons is formed.

7.4.4 Enzyme Catalysis

Living organisms carry out thousands of chemical reactions which take place in dilute solution at ordinary temperature and pressure. For example, they can use small molecules to assemble complex biopolymers such as proteins and DNA. Organisms can produce molecules that combat bacterial invaders. They can break down large, energy-rich molecules in many steps to extract chemical energy in small portions to drive their many activities.

Most of these reactions are catalysed by biochemical catalysts called *enzymes*. Enzymes are proteins with high molar mass ranging from 15,000 to 1,000,000 g/mol. Enzymes are incredibly *efficient catalysts*. They increase rates by 10^8 to 10^{20} times. Enzymes are also extremely *specific*: each reaction is generally catalysed by a particular enzyme. Urease, for example, catalyses only the hydrolysis of urea and none of the several thousand other enzymes present in the cell catalyses that reaction:

$$NH_2CONH_2 + H_2O \xrightarrow{urease} 2\ NH_3 + 2CO_2$$

The remarkable specificity of enzymes results from the fact that each enzyme has a specific, *active site* on its surface. When the reactant molecules, called the *substrates* of the reaction, bind at the active site, a chemical change is initiated. In most cases, *substrates bind to the active site through intermolecular* forces: H-bonds, dipole forces and other weak attractions.

Two models of enzyme action have been proposed (Fig. 7.8). According to the **lock-and-key model**, when the 'key (substrate) fits the 'lock' (active site), the chemical change begins. However, modern X-ray crystallographic and spectroscopic methods show that in many cases, the enzyme changes shape when the substrate lands at the active site. This *induced-fit model* of enzyme action pictures the substrate inducing the active site to adopt a perfect fit, rather than a rigidly shaped lock and key. Therefore, we might picture a hand in a glove, in which the

'glove' (active site) does not attain its functional shape until the 'hand' (substrate) moves into place.

The kinetics of enzyme catalysis has many features in common with ordinary catalysis. In the enzyme catalysed reaction, substrate (S) and enzyme (E) form an intermediate enzyme-substrate complex (ES) whose concentration determines the rate of product (P) formation. The steps common to virtually all enzyme catalysed reactions are:

(1) $E + S \rightleftharpoons ES$ (fast, reversible)

(2) $ES \rightarrow E + P$ (slow, rate determining)

The rate of enzyme catalysed reaction changes from first-order to zero-order as the concentration of substrate is increased (Unit 6).

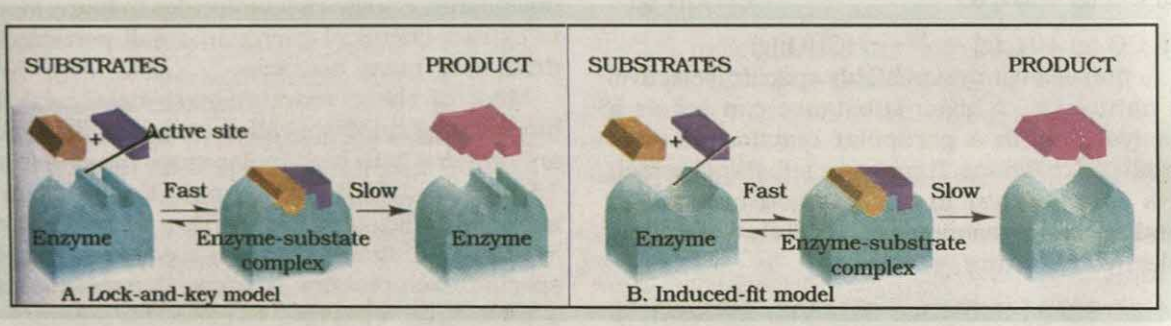


Fig. 7.8 *Two models of enzyme action. A. In the lock-and-key model, the active site is thought to be an exact fit for the substrate shape. B. In the induced-fit model, the active site is thought to change shape to fit the substrate. Most enzyme-catalysed reactions proceed through a fast, reversible formation of an enzyme-substrate complex, followed by a slow conversion to product and free enzyme.*

7.5 COLLOIDS

We have learnt in Unit 3 that solutions are homogeneous systems while we also know that if sand is stirred in water, it slowly settles down and is called a suspension.

Between the extremes of suspensions and solutions is a large group of systems called **colloidal dispersions** or simply **colloids**. A colloid is a heterogeneous system in which one substance is dispersed (**dispersed phase**) as very fine particles in another substance called **dispersion medium**. The essential difference between a solution and a colloid is one of particle size.

- In a solution, the particles are ions or small molecules.
- In a colloid, the dispersed phase may consist of particles of a single macromolecule (such as protein or synthetic polymer) or an aggregate of many atoms, ions or molecules. Colloidal particles are larger than simple molecules but small enough to remain suspended. They have a range of diameters between 1 and 1000 nm (10^{-9} to 10^{-6} m).

Colloidal particles have an enormous surface area per gram as a result of their small size. Consider a cube with 1 cm sides. It has a total surface area of 6 cm^2. If it were divided equally into 10^{12} cubes, the cubes would be the size of large colloidal particles and have a total surface area of 60,000 cm^2 or 6 m^2. This enormous surface area leads to some special properties of colloids to be discussed later in this Unit.

7.6 CLASSIFICATION OF COLLOIDS

Colloids are classified on the basis of the following criteria:

A. Physical state of dispersed phase and dispersion medium.

B. Nature of interaction between dispersed phase and dispersion medium.

C. Type of particles of the dispersed phase.

7.6.1 Classification Based on Physical State of Dispersed Phase and Dispersion Medium

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gases, **eight types of colloidal systems are possible**. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system. The examples of the various types of colloids along with their typical names are listed in Table 7.3.

Many familiar commercial products and natural objects are colloids. For example, whipped cream is a foam, a gas dispersed in a

liquid. Firefighting foams, used at emergency airplane landings are also colloidal systems. Most biological fluids are aqueous sols (solids dispersed in water). Within a typical cell, proteins and nucleic acids are colloidal-sized particles dispersed in an aqueous solution of ions and small molecules.

Table 7.3 Types of Colloidal Systems

Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses, and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide-sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap-lather

Out of the various types of colloids given in Table 7.3, the most common are *sols* (solids in liquids), *gels* (liquids in solids) and *emulsions* (liquids in liquids). However, in the present Unit, we shall take up discussion of the 'sols' and 'emulsions' only. Further, it may be mentioned that if the dispersion medium is water, the sol is called **aquasol** or **hydrosol** and if the dispersion medium is alcohol, it is called **alcosol** and so on.

7.6.2 Classification Based on Nature of Interaction between Dispersed Phase and Dispersion Medium

Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two categories, namely, **lyophilic** (solvent attracting) and **lyophobic** (solvent repelling). If water is the dispersion medium, the terms used are *hydrophilic* and *hydrophobic*.

1. Lyophilic colloids: The word 'lyophilic' means *liquid-loving. Colloidal sols directly formed by substances like gum, gelatine, starch, rubber etc. on mixing with a suitable liquid (the dispersion medium) are called lyophilic sols.* An important characteristic of these sols is that if the dispersion medium is separated from the dispersed phase (say by evaporation), the sol can be reconstituted by simply remixing with the dispersion medium. That is why these sols are also called **reversible sols**. Furthermore, these sols are quite stable and cannot be easily coagulated.

2. Lyophobic colloids: The word 'lyophobic' means *liquid-hating. Substances like metals, their sulphides etc. when simply mixed with the dispersion medium do not form the colloidal sol. Their colloidal sols can be prepared only by special methods (as discussed later). Such sols are called lyophobic sols.* These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking and hence are not stable. Further, once precipitated, they do not give back the colloidal sol by simple addition of the dispersion medium. Hence, these sols are also called **irreversible sols**. Lyophobic sols need stabilising agents for their preservation.

7.6.3 Classification Based on Type of Particles of the Dispersed Phase: Multimolecular, Macromolecular and Associated Colloids

Depending upon the type of the particles of the dispersed phase, colloids are classified as: multimolecular, macromolecular and associated colloids.

1. Multimolecular colloids: When on dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size (with diameters less than 1 nm) in the colloidal range, the species thus formed are called **multimolecular colloids**. For example, a gold sol may contain particles of various sizes having many atoms. Sulphur sol consists of particles containing a thousand or more of S_8 sulphur molecules.

2. Macromolecular colloids: Macro molecules have large molecular masses (Unit 17). These on dissolution in a suitable solvent form a solution in which the size of the macromolecules may be in the colloidal range. Such systems are

called **macromolecular colloids**. These colloids are quite stable and resemble true solutions in many respects.

Examples of naturally occurring macromolecules are starch, cellulose, proteins, and enzymes. Examples of man-made macromolecules are polyethene, nylon, polystyrene, synthetic rubber, etc.

3. Associated colloids (Micelles): *There are some substances which at low concentrations behave as normal, strong electrolytes but at higher concentrations exhibit colloidal behaviour due to the formation of aggregated particles.* The aggregated particles thus formed are called **micelles**. These are also known as **associated colloids**. The formation of micelles takes place only above a particular temperature called **Kraft Temperature** (T_k) and above a particular concentration called **Critical Micelle Concentration (CMC)**. On dilution, these colloids revert back to individual ions. Surface active agents such as soaps and synthetic detergents belong to this class. For soaps, the CMC is ~ 10^{-4} to 10^{-3} mol L^{-1}. These colloids have both lyophobic and lyophilic parts. Micelles may contain as many as 100 molecules or more.

Mechanism of micelle formation: Let us take the example of soap solutions. Soap is sodium salt of a higher fatty acid and may be represented as $RCOO^-Na^+$ e.g., sodium stearate viz. $CH_3(CH_2)_{16}COO^-Na^+$ which is a major component of many bar soaps. When dissolved in water, it dissociates into $RCOO^-$ and Na^+ ions. The $RCOO^-$ ions, however, consist of two parts i.e., long hydrocarbon chain R (also called non-polar 'tail') which is hydrophobic (water repelling) and the polar group COO^- (also called polar-ionic 'head') which is hydrophilic (water loving). The $RCOO^-$ ions are, therefore, present on the surface with their COO^- groups in water and the hydrocarbon chains R staying away from it, and remain at the surface, but at higher concentration these are pulled into the bulk of the solution and aggregate in a spherical form with their hydrocarbon chains pointing towards the centre with COO^- part remaining outward on the surface. An aggregate thus formed is known as '**ionic micelle**'. These micelles may contain as many as upto 100 such ions.

Similarly, in case of detergents, e.g., sodium lauryl sulphate viz. $CH_3(CH_2)_{11}SO_4^-Na^+$, the polar group is $-SO_4^-$ along with the long hydrocarbon chain. Hence, the mechanism of micelle formation is same as that of soaps.

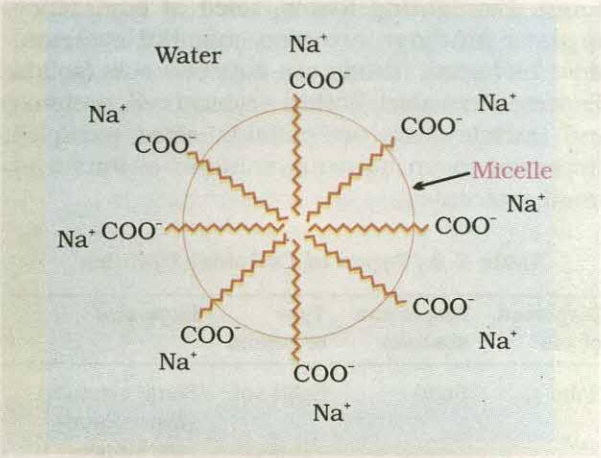


Fig. 7.9 *Aggregation of $RCOO^-$ ions to form an ionic micelle.*

7.7 PREPARATION OF COLLOIDAL SOLS

For the preparation of lyophobic and lyophilic sols different methods are employed:

A. Preparation of Lyophobic sols

Lyophobic sols can be prepared by two types of methods:

1. **Condensation methods**;
2. **Dispersion methods**.

1. Condensation methods

In these methods particles of atomic or molecular size are induced to combine to form aggregates having colloidal dimensions. For this purpose chemical as well as physical methods can be applied.

(a) Chemical methods. Colloidal solutions can be prepared by chemical reactions leading to formation of molecules by double decomposition, oxidation, reduction or hydrolysis. These molecules then aggregate leading to formation of sols.

$$As_2O_3 + 3H_2S \xrightarrow{\text{Double decomposition}} As_2S_3(sol) + 3H_2O$$

$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} 3S(sol) + 2H_2O$$

$$2\,AuCl_3 + 3\,HCHO + 3H_2O \xrightarrow{\text{Reduction}} 2Au(sol) + 3HCOOH + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3\,(sol) + 3HCl$$

(b) Physical methods

(i) Exchange of solvent: When a solution is mixed with an excess of the other solvent in

The Cleansing Action of Soaps

It has been mentioned earlier that a miscelle consists of a hydrophobic hydrocarbon like central core. The cleansing action of soap is due to these micelles, because oil and grease can be solubilised in their hydrocarbon, like centres which are not otherwise soluble in water. This is shown diagrammatically in Fig. 7.10. The dirt goes out along with the soap miscelles.

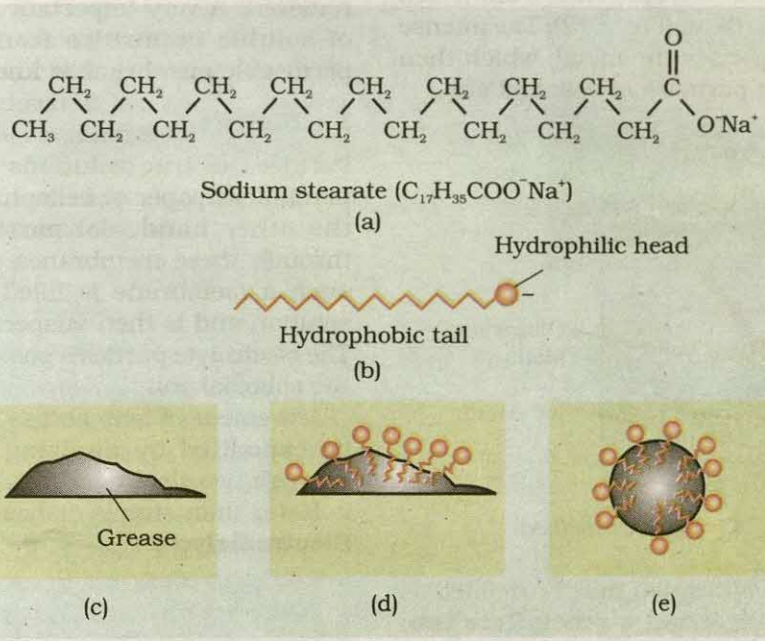


Fig. 7.10 *The cleansing action of soap. (a) A sodium stearate molecule (b) The simplified representation of the molecule that shows a hydrophilic head and a hydrophobic tail (c) Grease (oily substance) is not soluble in water (d) When soap is added to water, the non-polar tails of soap molecules dissolve in grease (e) Finally, the grease is removed in the form of micelles containing grease.*

which the solute is insoluble but solvent is miscible, a colloidal sol is obtained. For example, when a solution of sulphur in alcohol is poured in excess of water, a colloidal sol of sulphur is obtained.

(ii) Excessive cooling: The colloidal sol of ice in an organic solvent such as $CHCl_3$ or ether can be obtained by freezing a solution of water in the solvent. The molecules of water which can no longer be held in solution separately combine to form particles of colloidal size.

2. Dispersion Methods

In these methods large particles of the substance are broken into particles of colloidal dimensions in the presence of dispersion medium. These are stabilized by adding some suitable stabilizer. Some of the methods employed for carrying out dispersion are given below:

(a) Mechanical dispersion: In this method, the coarse suspension of the substance is brought into a colloidal state in the dispersion medium by grinding it in a colloid mill (Fig. 7.11), ball mill or ultrasonic disintegrator. The colloid mill consists of two metal discs, close together, rotating at high speed (7,000 revolutions per minute) in opposite directions. The suspension particles are torn off to the colloidal size.

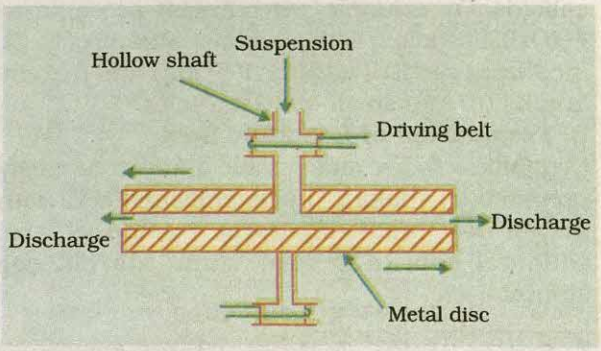


Fig. 7.11 *A colloid mill.*

(b) Electrical disintegration or Bredig's Arc method: This process involves dispersion as well as condensation. Colloidal sols of metals such as gold, silver, platinum, etc., can be prepared by this method. In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium (Fig. 7.12). The intense heat produced vaporises the metal, which then condenses to form particles of colloidal size.

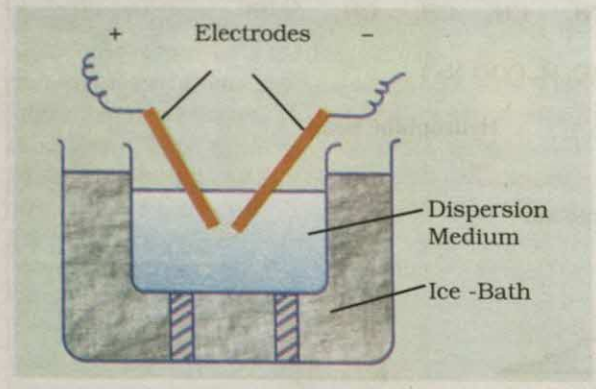


Fig 7.12 Bredig's Arc method.

(c) Peptization: Peptization may be defined as the **process of converting a precipitate into colloidal sol** by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called **peptizing agent**. This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol.

During peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface. The ion adsorbed on the surface is common either with the anion or cation of the electrolyte. This causes the development of positive or negative charge on precipitates which ultimately break up into smaller particles having the dimensions of colloids. For example, when freshly precipitated $Fe(OH)_3$ is shaken with aqueous solution of $FeCl_3$ (peptizing agent) it adsorbs Fe^{3+} ions and thereby breaks up into small-sized particles.

B. Preparation of Lyophilic Sols

Lyophilic sols are quite stable and can be easily prepared by shaking the lyophilic material with dispersion medium. Some examples are: colloidal sols of gelatin, gum, starch, egg albumin, etc.

7.8 PURIFICATION OF COLLOIDAL SOLS

The colloidal sols obtained by various methods are impure and contain impurities of electrolytes and other soluble substances. These impurities may destabilise the sol. Hence, they have to be removed. A very important method of removal of soluble impurities from sols by a semi-permeable membrane is known as **dialysis**[3].

1. Dialysis

Particles of true solutions can pass through parchment paper or cellophane membrane. On the other hand, sol particles cannot pass through these membranes. A bag made up of such a membrane is filled with the colloidal solution and is then suspended in fresh water. The electrolyte particles pass out leaving behind the colloidal sol.

Movement of ions across the membrane can be expedited by applying electric potential through two electrodes (Fig. 7.13). This method is faster than simple dialysis and is known as **Electrodialysis**.

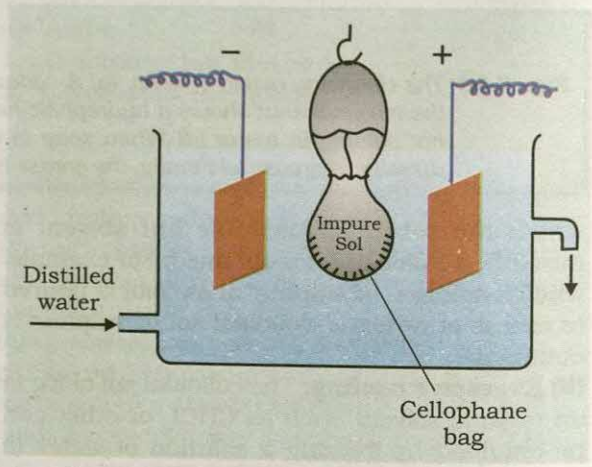


***Fig. 7.13** An apparatus for electrodialysis.*

2. Ultra-filtration

In this method, colloidal sols are purified by carrying out filtration through special type of graded filters called ultra-filters. These filter papers allow only the electrolytes to pass through. These filter papers are made of particular pore size by impregnating ordinary

[3] *The most important application of dialysis is in the purification of blood with the help of artificial kidney machine. The dialysis membrane permits excess ions and waste products like urea molecules to pass through whereas colloid sized particles of haemoglobin etc. do not pass through the membrane.*

filter paper with colloidal particles. In order to accelerate the filtration through such filter papers, increased pressure or suction is employed.

3. Ultra-centrifugation

In this method, the colloidal sol is taken in a tube which is placed in an ultra-centrifuge. On rotation of the tube at high speeds, the colloidal particles settle down at the bottom of the tube and the impurities remain in the solution called the centrifugate. The settled colloidal particles are mixed with an appropriate dispersing medium to regenerate the sol.

7.9 IMPORTANT PROPERTIES OF COLLOIDAL SOLS

1. Colligative Properties

Colloidal sols show the colligative properties viz. relative lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure. However, due to high average molecular masses of colloidal particles, mole fraction of the dispersed phase is very low. Hence, the values of the colligative properties observed experimentally are very small. Only osmotic pressure measurements are used in determining the molecular mass of polymers.

2. Optical Properties-Tyndall effect

Tyndall, in 1869, observed that if a strong beam of light is passed through a colloidal sol placed in a dark place, the path of the beam gets illuminated (Fig. 7.14). This phenomenon is called **Tyndall effect**, which is due to the scattering of light by the colloidal particles. The illuminated path of beam is called **Tyndall cone**.

The same phenomenon is noticed due to scattering of light by dust particles, when a beam of sunlight enters a dark room through a slit. Mist pierced by headlights at night also displays the same effect.

True solutions do not exhibit Tyndall effect because the particles in them are too small in size and do not cause any scattering.

3. Mechanical Properties

Brownian movement: Robert Brown, a botanist, discovered in 1827 that pollen grains placed in water do not remain at rest but move about continuously and randomly. Later on, this phenomenon was observed in case of colloidal

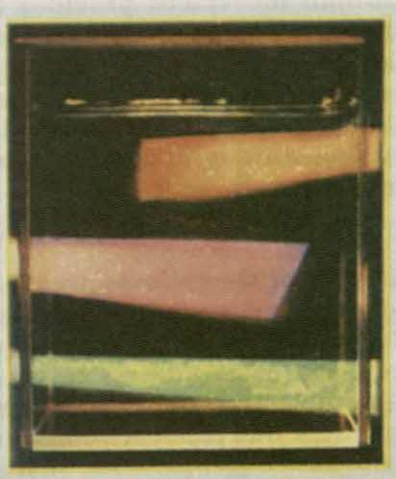


Fig. 7.14

Fig. 7.14 *Three beams of white light passing through a colloid of sulphur particles in water change from orange to pink and bluish green. The colours produced depend on the size of the particles and also on the position of viewers. The smaller the particles, the shorter (bluer) the wavelength.*

particles when they were seen under an *ultramicroscope*. The particles were seen to be in constant *zig-zag* motion (Fig. 7.15). This *zig-zag* motion is called **Brownian movement**.

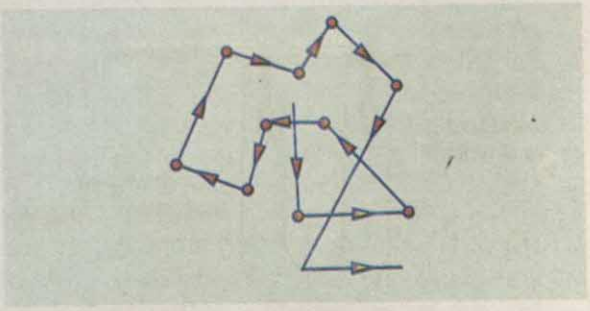


Fig. 7.15 *Brownian movement.*

Brownian movement arises because of the impact of the molecules of the dispersion medium with the colloidal particles. It has been postulated that the impact of the molecules of the dispersion medium on the colloidal particle are unequal leading to zig-zag motion. However, as the size of the particle increases, the effect of the impacts average out and the Brownian movement becomes slow. Ultimately, when the dispersed particle becomes big enough to acquire the dimensions of suspension, no Brownian movement is observed.

(i) Brownian movement provides a direct demonstration of ceaseless motion of molecules as postulated by kinetic theory.
(ii) It counters the force of gravity acting on colloidal particles and hence helps in providing stability to colloidal sols by not allowing them to settle down.

4. Electrical Properties: Electrophoresis

The particles of the colloids are electrically charged and carry positive or negative charge. The dispersion medium has an equal and opposite charge making the system neutral as a whole. Due to similar nature of the charge carried by the particles, they repel each other and do not combine to form bigger particles. That is why, **a sol is stable and particles do not settle down.** Arsenious sulphide, gold, silver and platinum particles in their respective colloidal sols are negatively charged while particles of ferric hydroxide, aluminium hydroxide are positively charged. The existence of the electric charge is shown by the phenomenon of **electrophoresis**. It involves the 'movement of colloidal particles either towards the cathode or anode, under the influence of the electric field'. The apparatus used for electrophoresis is shown in Fig. 7.16.

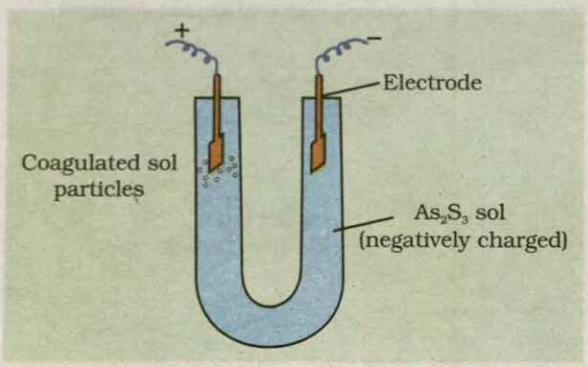


Fig. 7.16 *A set up for electrophoresis.*

The colloidal solution is placed in a U-tube fitted with platinum electrodes. On passing an electric current, the charged colloidal particles move towards the oppositely charged electrode. Thus, if arsenious sulphide sol is taken in the U-tube, its particles move towards the anode.

5. Coagulation of Colloids

The presence of small amounts of appropriate electrolytes is necessary for the stability of the colloids. However, when an electrolyte is added in larger concentration, the particles of the sol take up the ions which are oppositely charged and thus get neutralised. The neutral particles then start aggregating giving particles of larger size which are then precipitated. **This process of aggregation of colloidal particles into an insoluble precipitate by the addition of some suitable electrolyte is known as coagulation.** At lower concentration of electrolytes, the aggregation of particles is called **flocculation** that can be reversed on shaking while at higher concentration of electrolyte, coagulation takes place and the same cannot be reversed simply by shaking. When river water containing colloidal clay flows into the sea, electrolytes present in the brine induce coagulation. This is a major cause of silting in estuaries.

It needs to be noted that the coagulation of a colloidal solution by an electrolyte does not take place until the added electrolyte has certain minimum concentration in the solution. The minimum amount of an electrolyte (in millimoles) that must be added to one litre of a colloidal solution so as to cause its complete coagulation is called the **precipitation** or **coagulation value of the electrolyte**.

Different electrolytes have different coagulation values. The coagulation behaviour of various electrolytes was studied in detail by Hardy and Schulze. They found that

(i) *The ions carrying charge opposite to that of sol particles are effective in causing the coagulation of the sol.*
(ii) *Coagulating power of an electrolyte is directly proportional to the fourth power of the valency of the ions causing coagulation.*

Thus, for the coagulation of sols carrying negative charge (like As_2S_3 Sol), Fe^{3+} ions are more effective than Ba^{2+} or Na^+ ions. Similarly, for the coagulation of sols carrying positive charge (such as $Fe(OH)_3$ sol), PO_4^{3-} ions are more efficient than SO_4^{2-} or Cl^- ions. The two observations given above are collectively called **Hardy-Schulze rule.**

These observations show that utmost care should be taken to keep sols away from environment containing even small amounts of electrolytes.

7.10 EMULSIONS

Emulsions are colloids in which both dispersed phase and dispersion medium are liquids.

Emulsions can be broadly classified into two types:

(i) **Oil in water emulsions**: In this type of emulsions, oil acts as (organic solvent) dispersed phase and water acts as dispersion medium. Some examples of this type of emulsions are milk, vanishing cream, etc. In milk, liquid fat is dispersed in water.

(ii) **Water in oil emulsions**: In this type of emulsions, water acts as dispersed phase and oil (organic solvent) acts as dispersion medium. Cold cream, butter, cod liver oil, etc. are examples of oil emulsions.

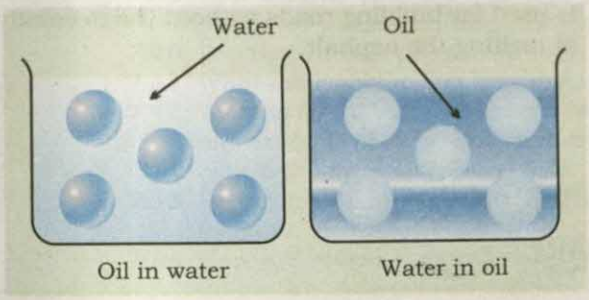


Fig. 7.17 Types of Emulsions.

7.10.1 Identification of Emulsion

The following tests may be employed to distinguish between the two types of emulsions:

(i) Dye test: Some oil soluble dye is added to the emulsion, if the background becomes coloured, the emulsion is water-in-oil type and if the coloured droplets are seen, the emulsion is oil-in-water type.

(ii) Dilution test: If the emulsion can be diluted with water, this indicates that water is the dispersion medium and the emulsion is of oil-in-water type. In case the added water forms a separate layer, the emulsion is water-in-oil type.

7.10.2 Preparation of Emulsions

Emulsification: The process of making an emulsion is known as **emulsification**. Emulsions may be obtained by vigorously mixing both the liquids. However, this gives an unstable emulsion. The dispersed drops at once come together and form separate layers. To stabilise an emulsion, the addition of a small quantity of a third substance known as **emulsifying agent** or **emulsifier** is essential. **Soaps and detergents are most frequently used as emulsifiers**. They coat the drops of an emulsion and check them from coming together and the emulsion is thus stabilised. The other common stabilising agents are proteins, gum and agar. The type of emulsion formed depends upon the relative amounts of the two liquids. If water is in excess, it is oil-in-water emulsion. If on the other hand, oil is in excess, it is water-in-oil emulsion. The type of emulsion formed also depends upon the nature of the emulsifying agent. For example, the presence of soluble soaps as the emulsifying agent generally favours the formation of emulsions of oil-in-water type, whereas the presence of insoluble soaps (containing non-alkali metal atoms) favour the formation of emulsions of water-in-oil type.

Demulsification: The separation of an emulsion into its constituent liquids is called **demulsification**. The various techniques applied for demulsification are freezing, boiling, centrifugation, electrostatic precipitation or chemical methods which destroy the emulsifying agents.

7.11 APPLICATIONS OF COLLOIDS

Colloids including emulsions find a number of uses in our daily life and industry. Some of the uses are given below.

1. Rubber plating: The negatively charged rubber particles from rubber sol are deposited on wares and handles of different tools. Rubber gloves are formed by rubber plating on suitable templates.

2. Sewage disposal: Sewage water contains charged colloidal particles of dirt, rubbish, etc., and these do not settle down easily. The particles can be removed by discharging them at electrodes. Dirty water is passed through a tunnel fitted with metallic electrodes which are maintained at high potential difference. The particles migrate to the oppositely charged electrode, lose their charge and get coagulated. The deposited matter is used as a manure and the water left behind is used for irrigation.

3. Cottrell smoke precipitator: Smoke is a dispersion of negatively charged colloidal particles of carbon in air and can be made free of these colloidal particles by passing it through **cottrell precipitator** (Fig. 7.18) installed in the chimney of an industrial plant. It consists of two metal discs charged to a high potential. The carbon particles get discharged and precipitate, while gases come out from the chimney.

4. Preparation of nano-materials: These materials are prepared for use as catalyst by using reverse micelles.

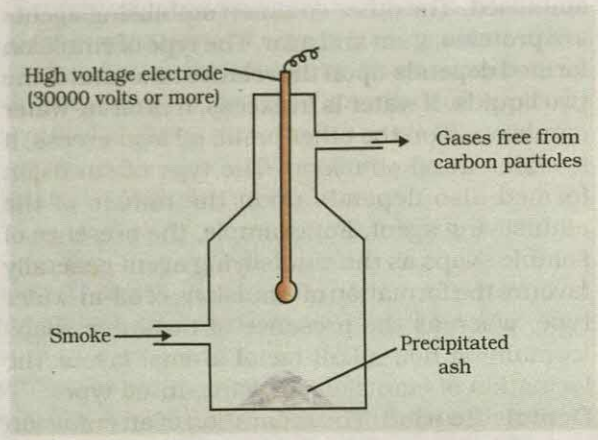


Fig. 7.18 *Cottrell smoke precipitator.*

5. In medicines: A wide variety of medicinal and pharmaceutical preparations are emulsions. It is believed that in this form they can be more effective and are easily assimilated.

6. In disinfectants: The disinfectants such as dettol and lysol give emulsions of the oil-in-water type when mixed with water.

7. In metallurgical operations: Emulsions play an important role in industry. The metal ores are concentrated by froth-floatation process which involves the treatment of the pulverised ore in emulsion of pine oil.

8. Building roads: Asphalt emulsified in water is used for building roads without the necessity of melting the asphalt.

SUMMARY

Adsorption is the phenomenon of attracting and retaining the molecules of a substance on the surface of a solid or a liquid resulting into a higher concentration on the surface. The substance adsorbed is known as **adsorbate** and the substance on which adsorption takes place is called **adsorbent**. In physisorption, adsorbate is held to adsorbent by weak van der Waals forces, and in chemisorption, adsorbate is held to adsorbent by strong chemical bond. Almost all solids adsorb gases. The extent of adsorption of a gas on a solid depends upon nature of gas; nature of solid; specific area of the solid; pressure of gas; temperature of gas; and activation of adsorbent. The relationship between the magnitude of adsorption (x/m) and pressure of the gas at constant temperature is known as **adsorption isotherm**.

A **catalyst** is a substance which increases rate of a chemical reaction without getting itself used up in the reaction. The phenomenon is known as **catalysis**. In homogeneous catalysis, the catalyst is in the same phase as are the reactants, and in heterogeneous catalysis the catalyst is in the different phase than are the reactants.

Colloidal solutions are intermediate between true solutions and suspensions. The size of the colloidal particles ranges from 1 to 1000 nm. A colloidal system consists of two phases – the dispersed phase and the dispersion medium. Colloidal systems are classified in three ways depending upon (i) physical states of the dispersed phase and dispersion medium (ii) nature of interaction between the dispersed phase and dispersion medium, and (iii) nature of particles of dispersed phase. **Lyophobic sols** are prepared by two types of methods: (i) chemical methods, and (ii) dispersion methods. The colloidal systems show interesting optical, mechanical and electrical properties. The process of changing the colloidal particles in a sol into the insoluble precipitate by addition of some suitable electrolytes is known as **coagulation**. **Emulsions** are colloidal systems in which both dispersed phase and dispersion medium are liquids. These can be of: (i) **oil in water type**, and (ii) **water in oil type**. The process of making emulsion is known as **emulsification**. To stabilise an emulsion, an emulsifying agent or emulsifier is added. Soaps and detergents are most frequently used as emulsifiers.

EXERCISES

7.1 Distinguish between the meaning of the terms adsorption and absorption. Give one example of each.
7.2 What is the difference between physical adsorption and chemisorption?
7.3 Give reason why a finely divided substance is more effective as an adsorbent.
7.4 What are the factors, which influence the adsorption of a gas on a solid?
7.5 What is an adsorption isotherm? Distinguish between Freundlich adsorption isotherm and Langmuir adsorption isotherm.
7.6 What do you understand by activation of adsorbent? How is it achieved?
7.7 What role does adsorption play in heterogeneous catalysis?
7.8 Give two chemical methods for the preparation of colloids.
7.9 How are the colloidal solutions classified on the basis of physical states of the dispersed phase and dispersion medium?
7.10 Discuss the effect of pressure and temperature on the adsorption of gases on solids.
7.11 What are lyophilic and lyophobic sols? Give one example of each type.
7.12 What is the difference between multimolecular and macromolecular colloids? Give one example of each. How are associated colloids different from these two types of colloids?
7.13 Describe a chemical method each for the preparation of sols of sulphur and platinum in water.
7.14 How are colloids classified on the basis of (a) physical states of components, (b) nature of dispersion medium and (c) interaction between dispersed phase and dispersion medium?
7.15 Explain what is observed
(i) when a beam of light is passed through a colloidal sol.
(ii) an electrolyte NaCl is added to ferric hydroxide sol.
(iii) electric current is passed through a colloidal sol.
7.16 What are emulsions? What are their different types ? Give example of each type.
7.17 What is demulsification? Name two demulsifiers.
7.18 Action of soap is due to emulsification and micelle formation. Comment.
7.19 Give four examples of heterogeneous catalysis.
7.20 What do you mean by activity and selectivity of catalysts?
7.21 Describe some features of catalysis by zeolites.
7.22 What is shape selective catalysis?
7.23 Explain the following terms (1) Peptisation (2) Electrophoresis (3) Coagulation (4) Dialysis (5) Tyndall effect.
7.24 Give four uses of emulsions.
7.25 What are micelles? Give an example of a micelles system.
7.26 Explain the terms with suitable examples: (1) Gel (2) Aerosol and (3) Hydrosol.
7.27 Comment on the statement that "colloid is not a substance but a state of substance".

UNIT 8

THE *p*-BLOCK ELEMENTS

OBJECTIVES

After studying this Unit, you will be able to:

- appreciate the general trends in the chemistry of elements of groups 13, 14, 15, 16 and 17.
- describe the process of extraction of aluminium metal from bauxite.
- know about the allotropes of sulphur and the manufacture, reactions and uses of sulphuric acid.
- appreciate the close similarity in the properties of halogens.
- know the unique characteristics of Group 18 elements (noble gases): helium, neon, argon, krypton, xenon, radon and the chemistry of xenon.

"Silicon is the most abundant element in the earth's crust after oxygen, and together these 2 elements comprise 4 out of every 5 atoms available near the surface of the globe."

Groups 13 to 18 of the periodic table of elements constitute the *p*-block (Fig. 8.1). Despite the diverse nature of elements of this block, it is possible to make some useful generalizations regarding the trends in their properties (Fig. 8.2).

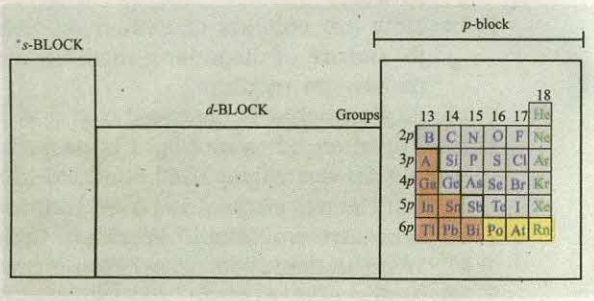


Fig. 8.1 *The location of p-block of elements in the periodic table.*

In Class XI, we learnt the chemistry of the first members B, C, N and O of groups 13 to 16 of the periodic table. In this Unit, we will have an overview of the chemistry of the remaining *p*-block elements with special reference to the individual chemistry of a few important elements and their compounds.

The *p*-block elements are characterised by the ns^2np^x valence shell electronic configurations (where x varies from 1 to 6 and *n* from 2 to 6). The inner core for different elements, however, differs. The highest oxidation state is numerically equal to the group number minus 10. On descending the group, the oxidation state two less than the highest group oxidation state becomes more stable in groups 13 to 16. This trend is termed the **inert pair effect**. The common oxidation states displayed by the *p*-block elements are shown in Table 8.1.

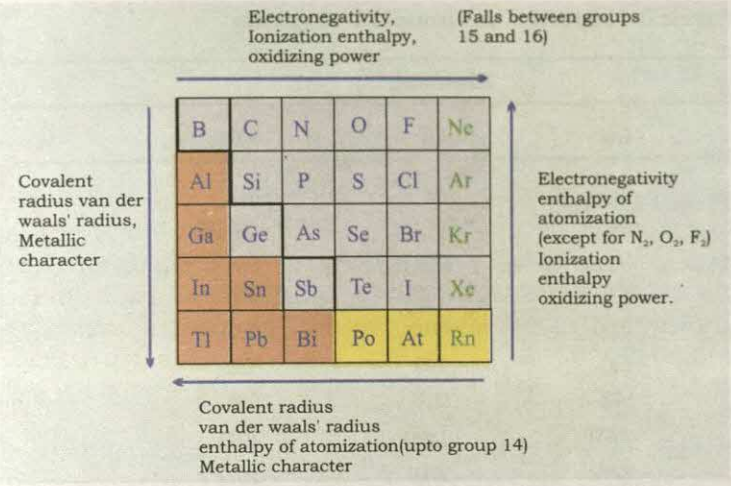


Fig. 8.2 *Trends in properties of p-block elements.*

We will now take up the systematic groupwise study of the *p*-block elements.

8.1 GROUP 13 ELEMENTS

Boron, aluminium, gallium, indium and thallium constitute the group 13 of the periodic table. In this Section, we will study briefly the trends in the properties of these elements and the chemistry of aluminium in detail.

8.1.1 Occurrence

Aluminium is the third most abundant element (8.3% by weight) in the earth's crust after oxygen (45.5%) and silicon (25.7%). The important minerals of aluminium are:

a) **bauxite**, $AlO_x(OH)_{3-2x}$ $(0 < x < 1)$;
b) **cryolite**, Na_3AlF_6;
c) **orthoclase**, $KAlSi_3O_8$;
d) **mica (muscovite)**, $KAl_2(Si_3AlO_{10})(OH)_2$;
e) **beryl**, $Be_3Al_2Si_6O_{18}$; and
f) **corundum**, Al_2O_3.

Bauxite is commercially the most important ore from which aluminium metal is extracted. Annual world production of bauxite exceeds 100 million tonnes out of which India produces 1 million tonnes.

Gallium, indium and thallium are less abundant than aluminium. Highest concentration (0.1-1%) of Ga is found in the rare mineral **Germanite** which is a complex sulphide of Zn, Cu, Ge and As. Indium and thallium occur in traces in sulphide ores of zinc and lead respectively.

8.1.2 Atomic and Physical Properties

The important atomic and physical properties of the elements of group 13 are given in Table 8.2. The atomic radius decreases from aluminium to gallium and increases again for In and Tl. The electronegativity decreases from B to Al but shows a slight increase for the heavier congeners. Unlike boron, the remaining elements of group 13 are all soft metals with low melting points and high electrical conductivity.

8.1.3 Oxidation States and Trends in Chemical Reactivity of Group 13 Elements

The common oxidation states, observed for group 13 elements, are +3 and +1(Table 8.1). The stability of the +1 oxidation state increases in the sequence Al < Ga < In < Tl. In aqueous solution Tl^+ is more stable than Tl^{3+} as shown by the redox potential data.

$Tl^{3+}(aq) + 2e^- = Tl^+(aq)$ $\quad E^\ominus = +1.25$ V

Table 8.1 Common oxidation states of *p*-block elements

Group	13	14	15	16	17	18
Oxidation State	B +3	C +4, – 4	N +5 to –3	O –1, –2	F –1	
	Al +3	Si +4	P, As +3, +5, –3	S, Se, Te –2, +2, +4, +6	Cl, Br, I –1, +1, +3 +5, +7	Xe +2, +4, +6, +8
	Ga, In, Tl +3, +1	Ge, Sn, Pb +4, +2	Sb, Bi +3, +5			

Table 8.2 Atomic and Physical Properties of Group 13 Elements

Property		Element				
		B	Al	Ga	In	Tl
Atomic number		5	13	31	49	81
Atomic mass		10.81	26.98	69.72	114.82	204.38
Electronic configuration		$[He]2s^2 2p^1$	$[Ne]3s^2 3p^1$	$[Ar]3d^{10} 4s^2 4p^1$	$[Kr]4d^{10} 5s^2 5p^1$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^1$
Atomic radius/pm [a]		85	143	135	167	170
Ionic radius M^{3+}/pm [b]		–	53.5	62.0	80.0	88.5
Ionic radius M^+/pm		–	–	120	140	150
Ionization enthalpy/	I	800	577	578	558	590
($kJ\ mol^{-1}$)	II	2427	1816	1979	1820	1971
	III	3659	2744	2962	2704	2877
Electronegativity [c]		2.0	1.5	1.6	1.7	1.8
Density/[$g\ cm^{-3}$ (293K)]		2.35	2.70	5.90	7.31	11.85
Melting point/K		2453	933	303	430	576
Boiling point/K		3923	2740	2676	2353	1730
$E^\ominus/V$ [d]		–	–1.66	–0.56	–0.34	+1.26
$E^\ominus/V$ [e]		–	0.55	–	–0.18	–0.34

[a] Metallic radius, [b] 6-coordination, [c] Pauling scale,
[d] For $M^{3+}(aq) + 3e^- \longrightarrow M(s)$ at 298 K; [e] For $M^+(aq) + e^- \longrightarrow M(s)$ at 298 K.

The relative stability of Tl^+ as compared to Tl^{3+} is an example of the inert pair effect referred to earlier. The term '**inert pair effect**' is somewhat misleading. The decreasing stability of the higher oxidation state (+3) with increasing atomic number arises because of the decrease in bond energy with size from aluminium to thallium. As a result, the energy required to unpair the ns^2 electrons is not compensated by the energy released in forming the two additional bonds.

The important trends observed in the chemical behaviour of group 13 elements are:

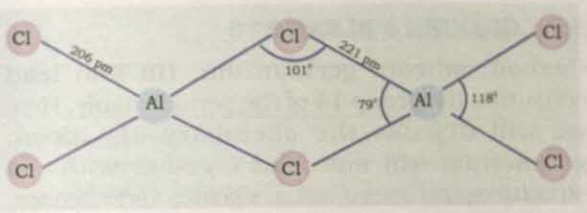
- Except boron, the other elements of group 13 show metallic character which increases down the group.
- Al, Ga, In and Tl exhibit a well-defined aqueous chemistry in their tripositive states. Species like $[M(OH)_4]^-$, $[M(H_2O)_2(OH)_4]^-$, $[M(OH_2)_6]^{3+}$ for M = Al, Ga, In, exist in aqueous solution.
- The group 13 elements form *hydrides* of the MH_3 type whose thermal stability decreases as we move down the group. AlH_3 is a solid, polymerised via Al - H - Al bridging units. These hydrides are weak Lewis acids and readily form adducts with strong Lewis bases (B:) to give compounds of the type MH_3: B (M= Al or Ga). They also form tetrahydrido anions, e.g., $[MH_4]^-$.

  The most important tetrahydrido compound is lithium tetrahydridoaluminate (III), $LiAlH_4$ which is obtained by the reaction:

  $$4\ LiH + AlCl_3 \xrightarrow{Et_2O} LiAlH_4 + 3\ LiCl$$

  $LiAlH_4$, a white crystalline solid and soluble in diethyl ether, is a versatile reducing agent used in organic synthesis.
- Al, Ga, In and Tl react with halogens to give binary halides. All the halides of group 13 elements are known except Tl(III) iodide. The fluorides are ionic and have high melting points. The chlorides, bromides and iodides are essentially covalent compounds with low melting points. These halides have halogen bridged dimeric structures as shown below for aluminium (III) chloride.

  The trihalides are strong Lewis acids. Anhydrous aluminium chloride is used as a catalyst in several organic reactions (Friedel - Crafts reaction).



of the type M_2O_3 and $M(OH)_3$, whose basic character increases as we move from aluminium to thallium. Aluminium and gallium hydoxides show amphoteric behaviour:

$$2Al(OH)_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 6H_2O(l)$$

$$Al(OH)_3(s) + NaOH(aq) \rightarrow Na[Al(OH)_4](aq)$$

In contrast to $Tl(OH)_3$ which is insoluble in water, Tl(OH) is soluble and is a strong base. Many of the Tl(I) compounds are similar to the corresponding alkali metal compounds.

- Al, Ga, In and Tl ions exist as octahedral aqua ions, $[M(OH_2)_6]^{3+}$ in aqueous solution and many salts like halides, sulphates, nitrates and perchlorates exist as hydrates. Aluminium sulphate forms double salts with sulphates of other metals and are called *alums*, having the general formula $MAl(SO_4)_2.12H_2O$, where M is a univalent cation, Na^+ or K^+. Alums are extensively used in the softening of hard water and as mordant in dyeing and printing of textiles. A mordant helps to bind the dye to the fabric.
- The (+1) oxidation state gets stabilised progressively from Ga to Tl. The monohalides, GaX, InX and TlX are known for X = Cl, Br and I. GaX and InX disproportionate in water:

$$3MX(s) \rightarrow 2M(s) + M^{3+}(aq) + 3X^-(aq)$$

Tl(I) is, however, stable.

Solution

Example 8.1
Which type of cations are capabale of replacing aluminium in alums? Give some examples.

The trivalent metal cations of about the same size as that of Al^{3+} are capable of replacing aluminium in alums. Examples: Ti^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+} and Co^{3+}.

8.1.4 Aluminium Metal Extraction

Aluminium metal is extracted from bauxite in a two-stage process. In the first stage, pure alumina (Al_2O_3) is obtained from bauxite and in the second stage, electrolysis of Al_2O_3 in molten cryolite (Na_3AlF_6) is carried out to obtain aluminium metal.

Bauxite contains SiO_2, iron oxides and titanium(IV) oxide as impurities. The bauxite ore is digested with a concentrated solution of sodium hydroxide at 473-523 K and 35-36 bar pressure. Aluminium oxide and silica dissolve to form sodium aluminate and sodium silicate respectively leaving behind iron oxide and TiO_2 which are filtered off.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$$

The filterate containing sodium aluminate and sodium silicate is diluted and seeded with freshly precipitated aluminium hydroxide which induces the precipitation of aluminium hydroxide leaving behind sodium silicate in solution.

$$Na[Al(OH)_4](aq) \xrightarrow{H_2O} Al(OH)_3(s) + NaOH(aq)$$

The aluminium hydroxide is filtered, dried and calcined at 1473 K to yield pure alumina. Aluminium is obtained from alumina by electrolysis; this is known as **Hall-Heroult process**. The modern electrolysis process uses synthetic cryolite, Na_3AlF_6. Typical electrolyte composition ranges are Na_3AlF_6(80-85%), CaF_2(5-7%), AlF_3(5-7%), Al_2O_3(2-8%-intermittently recharged). The electrolysis of this mixture is carried out in an electrolytic cell (schematically shown in Fig. 8.3) using carbon electrodes. The oxygen liberated at the anode reacts with the carbon anode producing CO and CO_2. The overall reactions may be written as:

Aluminium oxide, Al_2O_3, exists in several different modifications. Dehydration of $Al(OH)_3$ below 1173 K gives γ-alumina which is polycrystalline with large surface area. It is used in chromatography and as catalyst support. The high-temperature form produced by heating Al_2O_3, above 1300 K), is α-alumina known as corundum. It is very hard and a refractory material used as an abrasive. Several gemstones (ruby, saphire, topaz, emerald) consist of Al_2O_3 with trace metal ion impurities (e.g., Cr, Fe, Ti) that impart colour to the mineral.

Cathode : $Al^{3+}(melt) + 3e^- \rightarrow Al(l)$

Anode : $C(s) + O^{2-}(melt) \rightarrow CO(g) + 2e^-$

$C(s) + 2O^{2-}(melt) \rightarrow CO_2(g) + 4e^-$

For each kg of aluminium produced, over 0.5 kg of the carbon anode is burnt away. Because of this, anodes need to be replaced periodically. World annual production of aluminium exceeds 17 million tonnes out of which India contributes about 1 million tonnes.

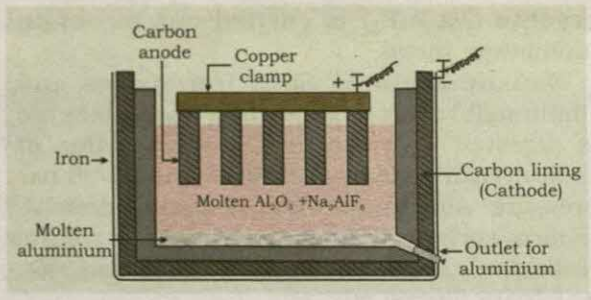


Fig. 8.3 *Electrolytic cell for the production of aluminium (schematic).*

Properties and uses of aluminium

Aluminium is a light silvery-white metal, with high tensile strength, a high electrical and thermal conductivity. On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper. It is highly electropositive and readily reacts with oxygen to form a hard protective layer of Al_2O_3, which renders it passive. Aluminium dissolves in aqueous hydrochloric acid to give:

$$2\,Al(s) + 6\,HCl(aq) + 12\,H_2O(l) \rightarrow 2\,[Al(H_2O)_6]Cl_3(aq) + 3\,H_2(g)$$

Nitric acid renders aluminium passive due to the formation of a protective layer of Al_2O_3 on its surface. Aluminium dissolves in strong alkali solutions to give aluminates liberating hydrogen:

$$2Al(s) + 2\,NaOH(aq) + 6\,H_2O(l) \rightarrow 2\,Na[Al(OH)_4](aq) + 3\,H_2(g)$$

Aluminium is used extensively in industry and everyday life. It forms many useful alloys with Cu, Mn, Mg, Si and Zn. Hence, aluminium and its alloys find use in packaging, utensil making, construction, aerospace and other transportation industries. It is used as a conductor for transmission of electricity. Aluminium is also used in the aluminothermic process for production of chromium and manganese from their ores (Class XI, Unit 10).

8.2 GROUP 14 ELEMENTS

Carbon, silicon, germanium, tin and lead constitute the group 14 of the periodic table. Here we will discuss the chemistry of silicon, germanium, tin and lead together with the structures and uses of silica, silicates and silicones, the extraction of tin and lead and preparation, properties and uses of their halides and oxides.

8.2.1 Occurrence and Uses

Silicon is present in nature in the form of **silica** (SiO_2) and **silicates**. Rocks and clays consist of silicate minerals. Silicon is the second most abundant element (~ 27.2 wt%) on the earth's crust, after oxygen (45.5 wt%). Germanium is a trace element (1.5 ppm) and is mainly recovered from flue dusts arising from the roasting of zinc ores. The natural abundances of tin and lead are 2 ppm and 13 ppm respectively. Tin occurs mainly as **cassiterite**, SnO_2. The principal ore of lead, **galena** (PbS) is often found in association with zinc blende (ZnS). Other ores of lead are **anglesite** ($PbSO_4$) and **cerussite** ($PbCO_3$). Small quantities of lead ores occur in Rajasthan. Silicon and germanium (though to a lesser extent) are used in the production of semiconductors and integrated circuits. Silicon is a very important component of ceramics, glass and cement. Ge is transparent in the infrared region and therefore is used in the making of infrared windows, prisms and lenses. Tin is used as a coating on metals and in making various alloys like solder, bronze and type metal. Lead is mostly used in storage batteries, in alloy making and pigments/chemicals.

8.2.2 Atomic and Physical Properties

The atomic and physical properties of group 14 elements are given in Table 8.3. These elements have the valence shell electronic configuration ns^2np^2. There is a considerable decrease in the ionization enthalpy as we move from carbon to silicon; thereafter, the variation is much less as the group is descended. The covalent and ionic radii increase steadily down the group. Tin and lead are soft metals with relatively low melting points (Table 8.3).

8.2.3 Silicon, Tin and Lead: Isolation of Silicon and its Properties

Elemental silicon is commercially produced by the reaction of sand (which is largely SiO_2) with

Table 8.3 Atomic and Physical Properties of Group 14 Elements

Property		Element C	Si	Ge	Sn	Pb
Atomic number		6	14	32	50	82
Atomic mass		12.01	28.09	72.60	118.71	207.2
Electronic configuration		$[He]2s^2 2p^2$	$[Ne]3s^2 3p^2$	$[Ar]3d^{10} 4s^2 4p^2$	$[Kr]4d^{10} 5s^2 5p^2$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^2$
Covalent radius/pm[a]		77	118	122	140	146
Ionic radius M^{4+}/pm[b]		–	40	53	69	78
Ionic radius M^{2+}/pm[b]		–	–	73	118	119
Ionization enthalpy/kJ mol^{-1}	I	1086	786	761	708	715
	II	2352	1577	1537	1411	1450
	III	4620	3228	3300	2942	3081
	IV	6220	4354	4409	3929	4082
Electronegativity[c]		2.5	1.8	1.8	1.8	1.9
Density[d]/g cm^{-3}		3.51[e]	2.34	5.32	7.26[f]	11.34
Melting point/K		4373	1693	1218	505	600
Boiling point/K		–	3550	3123	2896	2024
Electrical resistivity/ohm cm (293 K)		$10^{14} - 10^{16}$	50	50	10^{-5}	2×10^{-5}

[a] for M^{IV} oxidation state; [b] 6-coordination; [c] Pauling scale; [d] 293 K; [e] for diamond; for graphite, density is 2.22; [f] β-form (stable at room temperature)

coke in an electric furnace:

$$SiO_2 + 2C \xrightarrow{2273-2773\ K} Si + 2CO$$

Silicon obtained by this method is generally 96–98% pure and is mostly used in metallurgical industry to produce ferrosilicon and other alloys. Semiconductor grade silicon is prepared mainly by the reduction of highly pure $SiCl_4$ / $SiHCl_3$ with dihydrogen or by the pyrolysis of SiH_4. At room temperature silicon is unreactive towards all elements except fluorine. It combines with other halogens, nitrogen and elemental oxygen at high temperatures. Silicon forms carborundum (SiC) with carbon at high temperature. Carborundum which is extremely hard, is used as an abrasive and refractory material. Silicon dissolves in hot aqueous alkali to liberate hydrogen:

$$Si + 4\ OH^- \rightarrow SiO_4^{4-} + 2\ H_2$$

Extraction of tin and its properties

Tin is produced from **cassiterite** (SnO_2) by reducing it with carbon. The ore is crushed and washed with water to remove lighter impurities. It is then roasted to remove impurities such as arsenic and sulphur as volatile oxides. The roasted ore is heated with coal in a reverberatory furnace at 1500 K.

$$SnO_2 + 2\ C \longrightarrow Sn + 2\ CO$$

The crude tin obtained by this method is contaminated with iron and other metals. It is, therefore, remelted on an inclined surface. Tin, which has a lower melting point than other metallic impurities present, melts and flows down leaving behind the less fusible metals.

Tin is a soft silvery white metal. It is ductile and can be rolled into thin foils. Tin has two allotropes. The stable form at room temperature is the white tin, β-Sn, which transforms to grey tin, α-Sn, at 286K. White tin is not attacked by air or water at ordinary temperatures, heating with air or oxygen results in the formation of SnO_2. Tin readily reacts with halogens to form SnX_4. It is not attacked by dilute HCl or H_2SO_4 but dissolves in hot concentrated HCl or H_2SO_4 to yield $SnCl_2$ and $SnSO_4$ respectively. It reacts with hot alkali to form stannates, $M_2[Sn(OH)_6]$

$$Sn\ (s) + 2\ KOH\ (aq) + 4\ H_2O\ (l) \rightarrow K_2[Sn(OH)_6]\ (aq) + 2\ H_2\ (g)$$

Extraction of lead and its properties

Lead is normally obtained from **galena** (PbS). The ore is concentrated by froth-floatation and then roasted in a limited supply of air to give PbO which is reduced to the metal by heating with coke and limestone (flux) in a blast furnace.

Reduction of PbO with fresh galena (PbS) can also be used to obtain the metal. The molten lead is tapped from the bottom of the furnace.

$2\ PbS\ (s) + 3\ O_2\ (g) \rightarrow 2\ PbO(s) + 2\ SO_2(g)$

$PbO(s) + C(s) \rightarrow Pb\ (l) + CO(g)$

$PbO(s) + CO(g) \rightarrow Pb(l) + CO_2(g)$

$PbS\ (s) + 2\ PbO(s) \rightarrow 3\ Pb\ (l) + SO_2\ (g)$

Like tin, lead is a soft ductile metal which can be rolled into sheets and pipes. It has a bluish-grey appearance and a high density, nearly twice that of Sn. When exposed to air, it gets covered with a thin layer of lead hydroxide $Pb(OH)_2$ and $Pb(CO_3)$ and further reactivity is greatly decreased. Similarly, with concentrated H_2SO_4, an insoluble coating of $PbSO_4$ is formed and this protects the lead from further reacting with the acid.

8.2.4 Oxidation States and Trends in Chemical Reactivity

The common formal oxidation states observed for group 14 elements are +4 for silicon and +4 and +2 for Ge, Sn and Pb (Table 8.1). As in group 13, we come across the inert pair effect in this group also. The stability of the divalent state increases markedly in the sequence, Ge< Sn<Pb. In fact, the divalent state becomes dominant for Pb. Some important group trends are:

(a) On account of high ionisation enthalpies, simple M^{4+} ions of the group are not known.

(b) Unlike carbon, the other elements of the group form compounds having coordination numbers higher than 4 like $(SiF_5)^-$, $(SiF_6)^{2-}$ and $(PbCl_6)^{2-}$.

(c) In the divalent state, stable compounds of the type $M^{II}X_2$ for carbon and silicon are rare. The stability of the divalent state increases in the sequence, Ge < Sn < Pb.

(d) The tendency for **catenation** decreases drastically on moving from carbon to silicon and is further diminished as we go down the group. The decreasing order of catenation is C >> Si > Ge ≈ Sn > Pb, which may be attributed to the steady decrease in M-M bond strength.

(e) The ability to form $p\pi$-$p\pi$ multiple bonds to itself and to other elements, particularly nitrogen and oxygen, decreases drastically as we descend the group from carbon to lead. The reluctance of silicon to form $p\pi$-$p\pi$ bonds to itself is clearly shown by the following facts: that (i) elemental silicon exists only in the diamond structure and no form of elemental silicon is comparable to graphite and (ii) while CO_2 is a gas with two carbon-oxygen double bonds, SiO_2 is a solid and consists of an infinite three-dimensional network of Si-O single bonds (Section 8.2.5).

(f) Si, Ge, Sn and Pb form tetrahalides of the type MX_4. They are tetrahedral and essentially covalent. The ionic character and thermal stability of the halides decrease with increasing atomic number of the halogen, with the result that PbI_4 is virtually non-existent. They are hydrolysed readily by water, e.g.,

$SiCl_4 + 4\ H_2O \rightarrow Si(OH)_4 + 4\ HCl$

$SnCl_4 + 2\ H_2O \rightarrow SnO_2 + 4\ HCl$

Apart from tetrahalides, germanium, tin and lead form dihalides MX_2. The stability of the dihalides increases steadily in the sequence $CX_2 << SiX_2 << GeX_2 << SnX_2 < PbX_2$. Thus, the divalent state becomes more stable as we descend the group.

Tin(II) chloride is obtained by dissolving tin in concentrated HCl; when the solution is cooled, crystals of tin(II) chloride dihydrate $SnCl_2.2H_2O$ separate out. Anhydrous $SnCl_2$ is prepared by heating tin in a current of HCl vapour. $SnCl_2$ is used as a reducing agent in acid solution. For example, it reduces iron(III) to the iron(II) state:

$$2\ Fe^{3+} + Sn^{2+} \rightarrow Sn^{4+} + 2Fe^{2+}$$

Lead(II) halides are formed by adding halide ions to a soluble lead salt:

$$Pb^{2+} + 2X^- \rightarrow PbX_2\ (X = F, Cl, Br \text{ or } I)$$

Pb(II) halides are colourless solids except PbI_2, which is yellow. They are sparingly soluble in water. The formation of $PbCl_2$ and PbI_2 serves as a test for the detection of Pb^{2+} in qualitative analysis.

(g) Silicon, germanium, tin and lead form oxides of the composition $MO_2.SiO_2$ (silica) is an infinite three-dimensional network solid of silicon and oxygen atoms connected by single covalent bonds. In SiO_2, each silicon atom is bonded to four oxygen atoms in a tetrahedral arrangement. Three crystalline modifications of SiO_2 are **quartz**, **cristobalite** and **tridymite**, of which quartz and cristobalite are important. **Quartz** is used as a **piezoelectric material** (crystal oscillators and transducers). Several amorphous forms of silica such as *silica gel* and *fumed silica* are known. Silica gel is made by acidification

of sodium silicate and when dehydrated, is extensively used as a drying agent in chromatographic and catalyst support.

The dioxides GeO_2, SnO_2 and PbO_2 are all solids and exist in several modifications. While SiO_2 is acidic, GeO_2 and SnO_2 are amphoteric and PbO_2 is distinctly basic. Tin(IV) oxide can be prepared by heating elemental tin in oxygen or by treating it with concentrated HNO_3. SnO_2 is used as a polishing powder and also in the manufacture of glass and pottery. Lead(IV) oxide PbO_2 is prepared by treating trilead tetraoxide Pb_3O_4 with dilute HNO_3:

$$Pb_3O_4 + 4\ HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2\ H_2O$$

It is a powerful oxidising agent and liberates oxygen when treated with acids. Both Sn and Pb form stable monoxides, MO. SnO is obtained by heating tin oxalate:

$$SnC_2O_4 \rightarrow SnO + CO + CO_2$$

PbO exists in red, orange or yellow forms depending on the method of preparation. It can be prepared by heating lead(II) carbonate or lead(II) nitrate. Further heating of PbO in air in a reverberatory furnace at around 750 K gives Pb_3O_4 known as **red lead**. Red lead is a combination of Pb(II) and Pb(IV) oxides, i.e., $2PbO.PbO_2$.

Example 8.2

SiF_6^{2-} is known but $SiCl_6^{2-}$ is not. Why is it so?

Solution

The main reasons are:

(i) smaller size of F; steric repulsions will be less in SiF_6^{2-}

(ii) interaction of F lone pair electrons with Si is stronger than that of chlorine lone pairs.

8.2.5 Silicate Minerals

A large number of silicate minerals exist in nature. Some of these important minerals are: **feldspars**, e.g., Albite $NaAlSi_3O_8$, **zeolites**, e.g., chabazite $Ca_2[(AlO_2)_4(SiO_2)_8].H_2O]$, **micas** (muscovite) $[KAl_2(Si_3AlO_{10})(OH)_2]$ and **asbestos** $[Mg_3(Si_2O_5)(OH)_4]$. The basic structural unit in silicates is the SiO_4 tetrahedron. The SiO_4 tetrahedra can be linked in several different ways. Depending on the number of corners (0,1,2,3 or 4) of the SiO_4 tetrahedra shared, various kinds of silicates, single or double chains, rings, sheets or three-dimensional networks are formed. Some of the structural units found in silicates are shown in (Fig. 8.4).

Simple **orthosilicates** (e.g., Mg_2SiO_4) contain discrete SiO_4 units. When two SiO_4 tetrahedra share a corner (common oxygen atom), we get the $(Si_2O_7)^{6-}$ unit and the silicates are called **pyrosilicates**. When SiO_4 units share two oxygen atoms with each other, cyclic or linear single chain silicates having the empirical formula $[(SiO_3)^{2-}]_n$

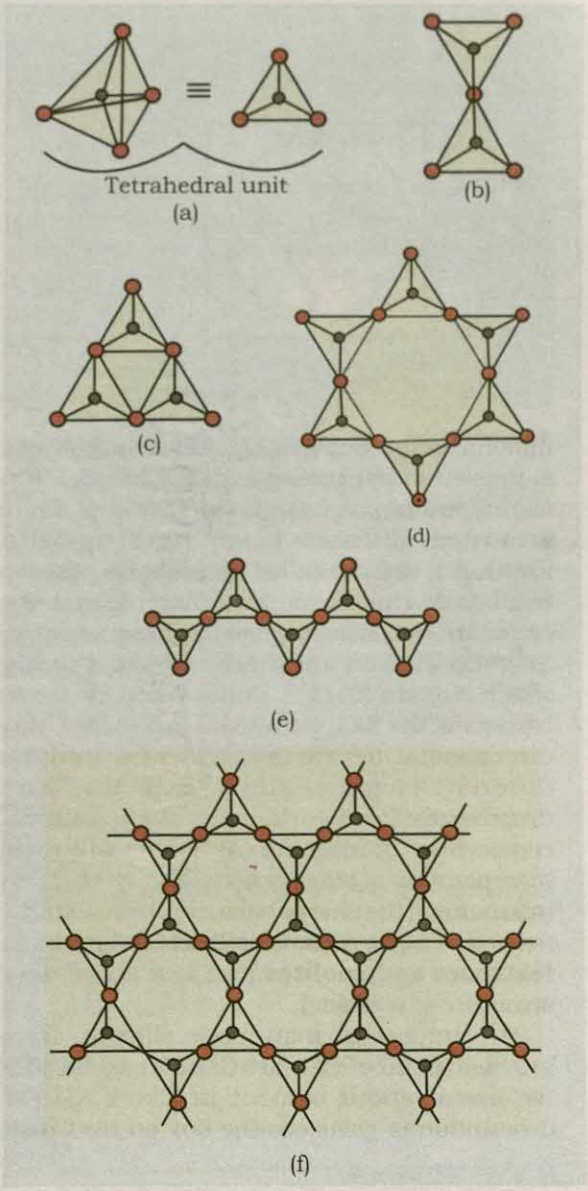
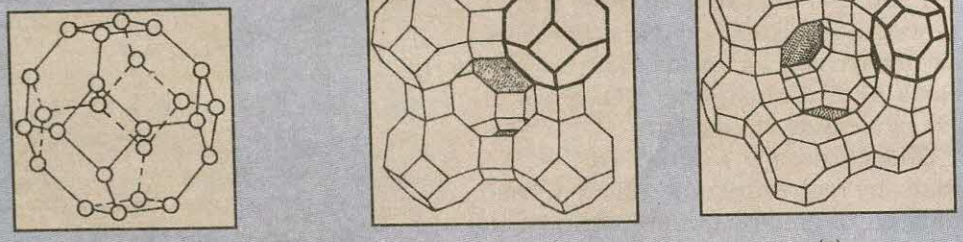


Fig. 8.4 *Some typical silicate structures: (a) $(SiO_4)^{4-}$ (b) $(Si_2O_7)^{6-}$ (c) $(Si_3O_9)^{6-}$ (d) $(Si_6O_{18})^{12-}$ (e) $(SiO_3^{2-})_n$ chain and (f) $(Si_2O_5^{2-})_n$ sheet.*

Zeolites

Zeolites are microporous aluminosilicates of general formula $M_{x/n}[AlO_2]_x[SiO_2].mH_2O$ and may be considered as open structures of silica in which aluminium has been substituted in a fraction x/(x+y) of the tetrahedral sites. The negative charge of the aluminosilicate framework is neutralized by exchangeable cations of valence n. The void space which can be greater than 50% of the volume, is occupied by m molecules of water in the unit cell. The truncated octahedron (cubo-octahedron) (a) is the building block of many zeolites. This is also called the b-cage or sodalite cage. Zeolites have high porosity due to the presence of one-, two- or three-dimensional network of interconnected channels and cavities of molecular dimensions. Accordingly, zeolite A shown as (b) is formed by linking sodalite cages through double four-membered rings. Faujasite (zeolite X and Y) is formed by linking the sodalite cages through double six-membered rings (c). Zeolite are used as molecular sieves and can separate molecules of different sizes. They are also used extensively as catalyst. (Please see section 7.6 of this book).



(a) (b) (c)

mineral, **beryl**, $Be_3Al_2Si_6O_{18}$. Linear silicate chain is present in **pyroxenes** (e.g. $MgCaSi_2O_6$). If two chains are cross- linked, the resulting double-stranded silicates have the composition $[(Si_4O_{11})^{6-}]_n$ and are called **amphiboles**. **Asbestos** belongs to this class. Two dimensional sheet structures are formed when three corners of each SiO_4 tetrahedron are shared as found in **clays** which contain $(Si_2O_5)^{2-}$ units. When all the four corners of the SiO_4 tetrahedra are shared, three-dimensional networks are formed leading to different forms of silica. If in this three-dimensional network, part of the silicon is replaced by aluminium (Al^{3+}), this will require incorporation of other cations (Na^+, K^+ or Ca^{2+}) for maintaining the charge balance. The resultant 3D frameworks give **Aluminosilicates** which include **feldspars** and **zeolites**.(See box above for the structure of a zeolite).

Two important man-made silicates from a practical point of view are GLASS and CEMENT. We learnt about cement in Class XI. For a description of glass see the box on next page.

8.2.6 Silicones

Another class of synthetic materials containing the Si–O–Si linkage are the **silicones**. These are polymers, which contain R_2SiO repeating units. The empirical formula is analogous to that of a ketone (R_2CO), hence these materials are named as **silicones.** They find a variety of applications because of their chemical inertness, water-repelling nature, heat resistance and good electrical insulating properties. They are used as sealants, greases, electrical insulators and for water-proofing of fabrics. Being bio-compatible they also find use as surgical and cosmetic implants.

Commercial silicone polymers are usually methyl derivatives and to a lesser extent phenyl derivatives. They are prepared by the hydrolysis of R_2SiCl_2 (R = Me or Ph).

$$R_2SiCl_2 \xrightarrow[-HCl]{H_2O} -O-\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{Si}}}}-O-\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{Si}}}}-O-\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{Si}}}}-O-$$

R = Me or Ph

The starting monomers, R_2SiCl_2 are industrially manufactured by the direct reaction of RCl with silicon in the presence of metallic copper as a catalyst.

$$2RCl + Si \xrightarrow[370\ K]{Cu\ powder} R_2SiCl_2$$

Glass

Ordinary glass is a mixture of sodium and calcium silicates and is made by heating a mixture of sand (essentially SiO_2) with sodium carbonate and calcium oxide in a furnace at around 1700 K and cooling it rapidly.

$$\underbrace{CaO + Na_2CO_3 + 6SiO_2}_{} \rightarrow \underbrace{Na_2SiO_3.CaSiO_3.4SiO_2}_{\text{glass}} + CO_2$$

This type of glass is called Soda lime glass or **soft glass** which has an approximate composition $Na_2SiO_3.CaSiO_3.4SiO_2$. Addition of small amounts of transition metal compounds to the glass mix. imparts colour to glasses. For example, Cr(III) and Mn(IV) compounds impart green and violet colours, respectively. **lead-potash glass** has a high refractive index and is used for making cut-glass objects and lenses for optical purposes. Addition of boric oxide or borax to replace part of SiO_2 results in the formation of heat-resistant **borosilicate glass** with a low coefficient of thermal expansion. This type of glass (trade name **pyrex/ corning/ Borosil**) can withstand sudden changes in temperature and is used for making laboratory glassware. Another route to glass formation is provided by the sol-gel process.

Glass is not a true solid, and has no definite melting point. It softens when heated to a certain temperature. It is a vitreous amorphous material. Though built up from SiO_4 tetrahedral units , their arrangement in glass is not regular as in crystalline silicates or in quartz.

8.3 GROUP 15 ELEMENTS

Group 15 of the Periodic table includes the elements nitrogen, phosphorus, arsenic, antimony and bismuth. There is a transition from non-metallic to metallic character as we go down the group. Nitrogen and phosphorus are non-metals; arsenic and antimony are semi-metals or metalloids; bismuth is metallic. Besides nitrogen, the other important element of group 15 is phosphorus. In this section we will learn the main group trends and the chemistry of phosphorus and its compounds.

8.3.1 Atomic and Physical Properties

The important atomic and physical properties of group 15 elements are listed in Table 8.4.

These elements have the ground state valence electronic configuration ns^2np^3. The covalent radius increases as we descend the group. Apart from nitrogen, the rest of the elements of this group have low and almost similar electronegativities. P, As, Sb and Bi are solids under normal conditions having several allotropic modifications.

8.3.2 Phosphorus: Occurrence, Isolation and Properties

In terms of its abundance (~ 1120 ppm), in the earth's crust, phosphorus occupies the eleventh place amongst elements. It occurs as phosphate rock which consists mainly of the minerals **hydroxyapatite**, $Ca_5(PO_4)_3(OH)$ and **fluorapatite**, $Ca_5(PO_4)_3F$. Vast deposits of

Table 8.4 Atomic and Physical Properties of Group 15 Elements

Property		N	P	As	Sb	Bi
Atomic number		7	15	33	51	83
Atomic mass		14.01	30.97	74.92	121.76	208.98
Electronic configuration		$[He]2s^22p^3$	$[Ne]3s^23p^3$	$[Ar]3d^{10}4s^24p^3$	$[Kr]4d^{10}5s^25p^3$	$[Xe]4f^{14}5d^{10}6s^26p^3$
Ionization enthalpy/(kJ mol^{-1})	I	1402	1012	947	834	703
	II	2856	1903	1798	1595	1610
	III	4577	2910	2736	2443	2466
Electronegativity		3.0	2.1	2.0	1.9	1.9
Covalent radius/pm[a]		70	110	120	140	150
Ionic radius/pm		171[b]	212[b]	222[b]	76[c]	103[c]
Melting point/K		63	317[d]	1089[e]	904	544
Boiling point/K		77.2	554[d]	888[f]	1860	1837
Density/[g cm^{-3}(298 K)]		0.879[g]	1.823	5.778[h]	6.697	9.808

[a] M^{III} single bond; [b] M^{3-}; [c] M^{3+}; [d] White phosphorus; [e] Grey α-form at 38.6 atm; [f] Sublimation temperature; [g] 63K [h] grey α-form

phosphate rock occur in North Africa and North America. In India, phosphate rock deposits are found in Rajasthan. Phosphorus is an essential constituent of animal and plant matter. It is present in bones (as inorganic phosphate) and also in living cells.

Elemental phosphorus is obtained by the reduction of calcined phosphate rock with coke and sand in an electric arc furnace at 1773 K. The overall reaction is represented as:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow P_4 + 6CaSiO_3 + 10CO$$

The phosphorus vapour thus obtained is condensed to a solid and stored under water to protect it from reaction with air. Annual world production of elemental P is 1.5 million tonnes of which India produces about 10,000 tonnes.

Allotropy of phosphorus

Phosphorus exhibits allotropy. The most common allotrope is **White phosphorus**, which is formed by condensation from the gaseous or liquid states. It is a waxy solid, which is insoluble in water but highly soluble in CS_2 and benzene. It is highly reactive and spontaneously ignites in air. Hence, it is stored under water. It glows in dark and this property gives the element its name PHOSPHORUS (Greek for 'light bringing'). *White phosphorus* consists of discrete P_4 molecules in which the four phosphorus atoms are at the corners of a tetrahedron and each phosphorus atom is covalently linked to the other three phosphorus atoms [Fig. 8.5(a)]. White phosphorus is highly toxic.

When white phosphorus is heated at 570 K in an inert atmosphere for several days, it gets converted into **red phosphorus** which has a higher melting point (870K) and greater density (~2.16 gcm^{-3}) than white phosphorus. Red phosphorus is amorphous and has a polymeric structure as shown in [Fig. 8.5(b)]. Red phosphorus is much less reactive than white phosphorus and is safer and easier to handle. It is essentially non-toxic.

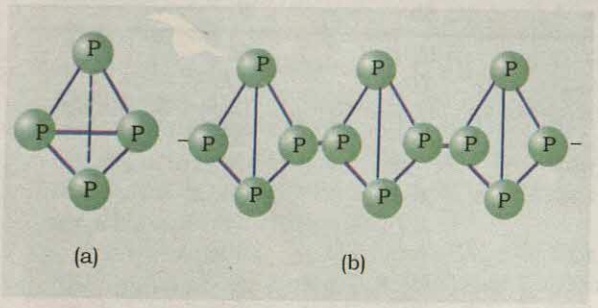


Fig. 8.5 *The structures of (a) white phosphorus and (b) red phosphorus. Note that in the former, there are discrete P_4 molecules while in the latter, P_4 units are linked in an extended chain structure.*

Thermodynamically, the most stable form of phosphorus is **black phosphorus**. It is obtained by heating WHITE PHOSPHORUS at 470 K under high pressure. A series of phases of black phosphorus are formed. One of these phases consists of an extended layer structure in which each P is bound to three neighbours by single bonds.

Uses of Phosphorus and its compounds

The major use of phosphorus is in the form of phosphatic fertilisers in agriculture (see later) and in the manufacture of food-grade phosphates, detergent phosphates and pharmaceuticals. Elemental phosphorus is the starting material for the manufacture of organo-phosphorus compounds used as pesticides.

8.3.3 Oxidation States and Trends in Chemical Reactivity of Group 15 Elements

The commonly observed oxidation states for phosphorus and arsenic are –3, +3 and +5. Antimony and bismuth generally display an oxidation state of +3 or +5 in its compounds (Table 8.1). The stability of the highest oxidation state (+5) decreases down the group. The +5 oxidation state in Bi is less stable than in Sb. The only well characterised Bi(V) compound is BiF_5.

Some trends observed in the chemical reactivity of group 15 elements are:

(a) Phosphorus displays essentially covalent character although it can accept three electrons to form phosphides. There is a decrease in covalent character in the sequence P > As > Sb > Bi.

(b) The heavier elements of this group (namely Sb and Bi) form M^{3+} cations due to decrease in ionisation enthalpy.

(c) For the heavier members of the group, the tendency to form double and triple bonds relative to single bonds diminishes markedly.

Thus, phosphorus, arsenic and antimony form tetrahedral E_4 molecules in their elemental state containing E-E single bonds. However, in the past two decades, a few stable compounds bearing E = X (X = C, N), E ≡ C and E = E (E, E′ = P, As, Sb or Bi) functionalities involving $p\pi$-$p\pi$ multiple bonds by the group 15 elements have been synthesised.

(e) In contrast to nitrogen, phosphorus shows a distinct tendency for catenation forming both cyclic and open chain compounds containing several phosphorus atoms.

(f) The heavier members of the group can form penta- and hexa-coordinated derivatives such as PCl_5, AsF_5 and PF_6^-.

8.3.4 Hydrides

All elements of group 15 form gaseous **hydrides** of the type MH_3. The stability of the hydrides decreases sharply on descending the group. Except NH_3, all the hydrides are strong reducing agents and react with metal ions (Ag^+, Cu^{2+}) to give phosphides, arsenides or antimonides. Phosphine and hydrides of other heavier members of the family are highly poisonous.

The preparative routes for group 15 hydrides are shown below:

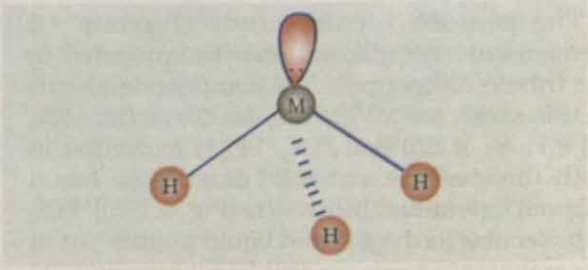
$$Ca_3P_2 + 6\ H_2O \rightarrow 2\ PH_3 + 3\ Ca(OH)_2$$

$$P_4 + 3\ KOH + 3\ H_2O \rightarrow PH_3 + 3\ KH_2PO_2$$

$$Zn_3M_2\,(s) + 6\ HCl\ (aq) \rightarrow 2\ MH_3\,(g) + 3\ ZnCl_2(aq)$$

M = As or Sb

Hydrides of group 15 elements show regular trends in their properties (Table 8.5). Unlike ammonia, PH_3 and other hydrides of group 15 elements are not associated (via hydrogen bonds) in the liquid state and are rather insoluble in water. PH_3 is a much weaker base than NH_3; AsH_3, SbH_3 and BiH_3 do not show any basic properties. These hydrides have a pyramidal structure.



M = N, P, As, Sb and Bi

8.3.5 Halides

Group 15 elements form two series of halides of the type MX_3 and MX_5. All the trihalides in the MX_3 series (M = P, As, Sb or Bi; X = F, Cl, Br or I) are known.

Bonding in the trihalo compounds is predominantly covalent except in the case of BiF_3. They are formed by the direct union of the elements with the halogens, keeping the group 15 elements in excess. PCl_3 is a colourless liquid with a boiling point of 349K. It fumes in moist air because of its reaction with water producing HCl.

$$PCl_3 + 3H_2O \longrightarrow 3\ H_3PO_3 + 3\ HCl$$

PCl_3 reacts with oxygen to form phosphoryl chloride, $P(O)Cl_3$. Like the hydrides, the trihalides of group 15 elements have a pyramidal structure in the gaseous state as shown for PF_3 in [Fig. 8.6(a)].

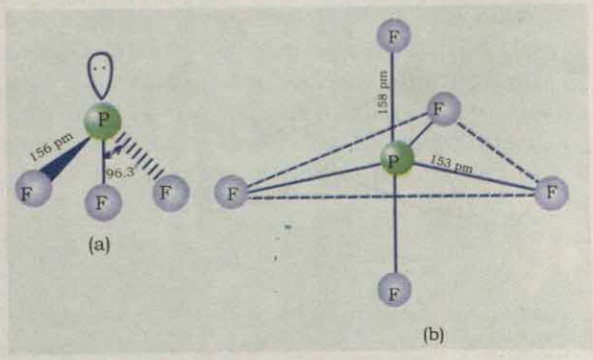


Fig. 8.6 The structures of (a) PF_3 and (b) PF_5 in the gas phase.

Table 8.5 Properties of Hydrides of Group 15 Elements

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point/K	195.2	139.5	156.7	185	–
Boiling point/K	238.5	185.5	210.6	254.6	290
(M – H) distance/pm	101.7	141.9	151.9	170.7	–
HMH angle (°)	107.8	93.6	91.8	91.3	–
$\Delta_f H^\ominus$/(kJ mol^{-1})	– 46.1	13.4	66.4	145.1	278
E(M-H)/(kJ mol^{-1})	391	322	247	255	–

The pentahalo compounds of group 15 elements are fewer in number as compared to the trihalo compounds. The compounds known in this series are MF_5(M = P, As, Sb or Bi), MCl_5 (M = P, As or Sb) and PBr_5. PF_5 is molecular in both the gaseous and solid states and has a trigonal bipyramidal structure [Fig. 8. 6(b)]. PCl_5 is molecular in the gas and liquid phases but in the solid state exists as $[PCl_4]^+[PCl_6]^-$ containing tetra and hexa-coordinated phosphorus species. Phosphorus pentachloride is the starting material for a variety of organophosphorus compounds and is made industrially by the reaction of PCl_3 with chlorine in CCl_4:

$$PCl_3 + Cl_2 \xrightarrow{CCl_4} PCl_5$$

PCl_5 fumes in air. It reacts with water to give initially $POCl_3$; if water is in excess, the product is H_3PO_4.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2\ HCl$$
$$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3\ HCl$$

Example 8.3
Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.

Solution
PCl_5 has a trigonal bipyramidal structure and the three equatorial P-Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds.

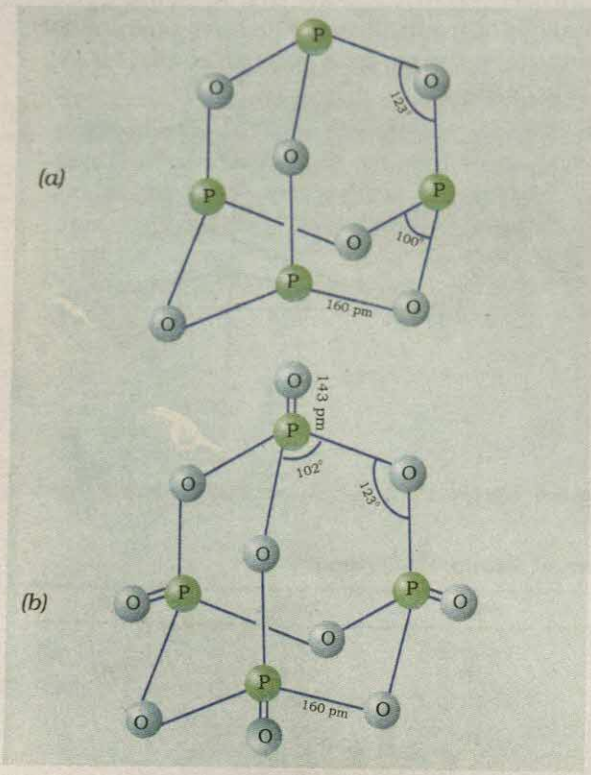


Fig. 8.7 *The structures of (a) phosphorus (III) oxide, P_4O_6 and (b) phosphorus(V) oxide, P_4O_{10}.*

8.3.6 Oxides

Phosphorus, arsenic, antimony and bismuth form two types of oxides: E_2O_3 and E_2O_5. The reluctance of P, As, Sb and Bi to enter into $p\pi$ - $p\pi$ multiple bonding leads to cage structures for their oxides and they exist as the dimers, E_4O_6 and E_4O_{10}. Bi(V) oxide is unstable. The structures of phosphorus(III) oxide, P_4O_6 and phosphorus(V) oxide, P_4O_{10} are shown in Fig. 8.7. The phosphorus atoms are at the corners of the tetrahedron as in white phosphorus. Six oxygen atoms are along the edges forming P-O-P single bonds.

The P(III), As(III) and Sb(III) oxides are prepared by heating the elements in a limited supply of oxygen, while the P(V) oxide, P_4O_{10} is obtained by burning white phosphorus in an excess of air or oxygen. Both P_4O_6 and P_4O_{10} are acidic oxides which dissolve in water to give *phosphonic acid* (phosphorous acid) and *phosphoric acid* (orthophosphoric acid) respectively.

$$P_4O_6 + 6\ H_2O \longrightarrow 4\ H_3PO_3$$
$$P_4O_{10} + 6\ H_2O \longrightarrow 4\ H_3PO_4$$

Because of its great affinity for water, P_4O_{10} is used as a dehydrating agent. It can dehydrate HNO_3 and H_2SO_4 to yield N_2O_5 and SO_3 respectively.

The basic nature of the oxides increases with increasing atomic number. Thus, P(III) and As(III) oxides are acidic; Sb(III) oxide is amphoteric and Bi(III) oxide is distinctly basic. Bi_2O_3 dissolves in acids to give salts:

$$Bi_2O_3 + 6\ HNO_3 \longrightarrow 2Bi(NO_3)_3 + 3H_2O$$

Among group 15 elements, Bi alone forms a stable nitrate, sulphate or carbonate and thus behaves like a metal.

8.3.7 Oxoacids of Phosphorus

Phosphorus forms numerous oxoacids, all of which are based on tetrahedral four coordinated phosphorus containing at least one P = O unit and one P – OH group. Some of the oxoacids of phosphorus are shown in Fig. 8.8. Two or more $P(O)(OH)_3$ units can join together to give what are known as condensed phosphoric acids having P – O – P links. They can have cyclic or

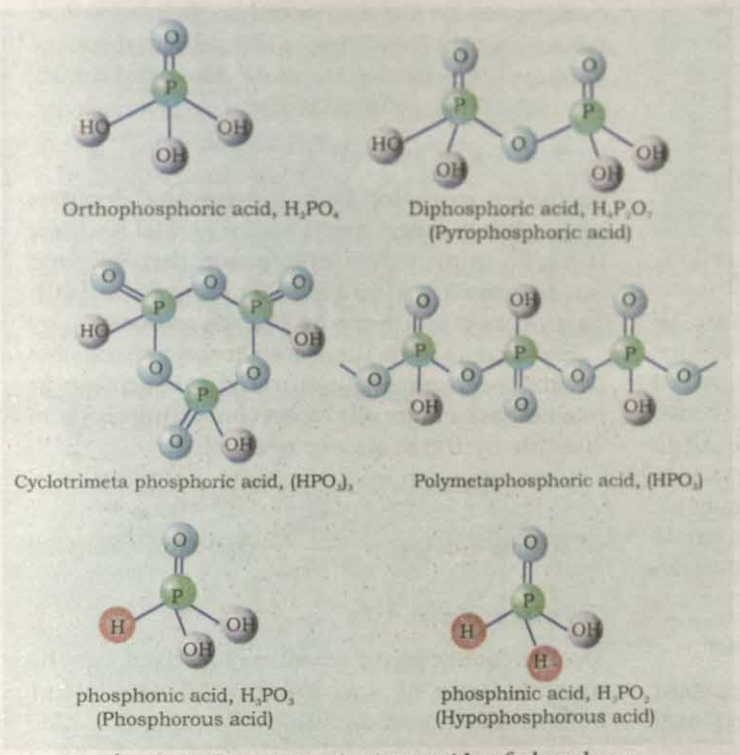


Fig. 8.8 *Some important oxoacids of phosphorus.*

linear chain structures. Salts of these acids are called condensed phosphates.

Phosphinic or **hypophosphorous acid, H_3PO_2**, has one P(OH) group and two hydrogens directly attached to phosphorus. It has only one ionisable hydrogen and hence behaves as a monoprotic acid. **Phosphonic** or **phosphorous acid** (H_3PO_3) has the structure, $HP(O)(OH)_2$ and is a diprotic acid forming two series of salts, NaH_2PO_3 and Na_2HPO_3. **Orthophosphoric acid** (H_3PO_4) is a triprotic acid; the successive pK_a values are 2.12, 7.2 and 12.4 at 298 K.

$$H_3PO_4 + H_2O \longrightarrow H_3O^+ + H_2PO_4^-$$
$$H_2PO_4^- + H_2O \longrightarrow H_3O^+ + HPO_4^{2-}$$
$$HPO_4^{2-} + H_2O \longrightarrow H_3O^+ + PO_4^{3-}$$

It forms three series of salts, e.g., NaH_2PO_4, Na_2HPO_4 and Na_3PO_4.

Orthophosphoric acid H_3PO_4, is a major industrial chemical. Bulk of this chemical is used for the manufacture of **phosphatic fertilisers** (see box given below). Pure acid is made by burning elemental phosphorus in air or oxygen, followed by action of water on P_4O_{10} so formed. The pure acid is used for the preparation of phosphate salts.

8.4 GROUP 16 ELEMENTS

Oxygen, sulphur, selenium, tellurium and polonium constitute the group 16 of the periodic table of elements. The first four elements are collectively called CHALCOGENS. The name derives from the Greek word for bronze and points to the association of sulphur and its congeners with copper. Polonium is radioactive and derives its name from Poland, the home country of Marie Curie who discovered the element in 1898. In this Section, we will study mainly the chemistry of sulphur and its compounds and also learn about some trends in the chemical properties of the group 16 elements.

Phosphatic Fertilizers

The fertility of soil can be enhanced by using chemical fertilisers which provide the essential plant nutrients, potassium, nitrogen and phosphorus. We learnt about the potassium and nitrogenous fertilisers in Class XI. Here we will briefly describe some of the phosphatic fertilizers.

The most important phosphatic fertiliser is the **superphosphate of lime**, $Ca(H_2PO_4)_2$. This is produced directly from phosphate rocks by treatment with concentrated sulphuric acid. In this way, insoluble phosphate rock is rendered soluble in water to improve the release of phosphorus to the soil for uptake by the plants.

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4$$

Phosphatic rock generally contains fluoride which reacts with H_2SO_4 to give hydrogen flouride, which in turn generates other side products. The gaseous side-products are removed by washing with water in a scrubber. Almost 90% of the phosphate rock mined goes into the production of phosphatic fertilisers; the remaining 10% is used for the production of elemental phosphorus.

Treatment of phosphate rock with phosphoric acid yields **triple super-phosphate**, $Ca(H_2PO_4)_2.H_2O$ which is free from calcium sulphate and hence contains a greater percentage of phosphorus:

$$Ca_5(PO_4)_3F + 7H_3PO_4 + 5H_2O \rightarrow 5Ca(H_2PO_4)_2.H_2O + HF$$

Phosphate Esters

Phosphate esters play a vital role in life processes. The most important of these biomolecules are DNA, RNA, adenosine mono-, di- and tri-phosphates (AMP, ADP and ATP) (Unit 17). Hydrolysis of P-O-P link in ADP releases energy which can be put to useful work.

8.4.1 Atomic and Physical Properties

The atomic and physical properties of group 16 elements are listed in Table 8.6. The valence shell electronic configuration of the group 16 elements is ns^2np^4, with each element two electrons short of the next noble gas configuration. The ionisation enthalpy decreases while the atomic and ionic radii increase as we descend the group. Unlike oxygen, which exists as a diatomic gas, the other group 16 elements exist as solids.

8.4.2 Occurrence, Extraction and Uses

Sulphur occurs in the earth's crust to the extent of 0.05% mostly as metal sulphides and sulphates. It also occurs in the elemental form in large underground beds. Another major source of sulphur is H_2S present in the natural gas and crude oil. Sulphur exists in combined state in living matter and is a constituent of some amino acids (e.g., cysteine), proteins and enzymes.

Selenium and tellurium are less abundant than sulphur (0.05 ppm in earth's crust for Se; 0.002 ppm for Te) and occur as selenides and tellurides in sulphide ores. The principal source of Se and Te is the 'anode slime' deposited during the electrolytic refining of Cu.

Extraction of sulphur

Sulphur is extracted from underground deposits by pumping superheated steam (~ 440 K) down the beds to melt the element and then blowing out the molten sulphur with compressed air. This process is known as **Frasch process**.

Sulphur is also recovered from natural gas by first separating H_2S through absorption in monoethanolamine and then converting H_2S into sulphur by the sequence of reactions:

$$H_2S + 3/2\ O_2 \longrightarrow SO_2 + H_2O$$

$$2H_2S(g) + SO_2(g) \xrightarrow[673\ K]{Fe_2O_3\ catalyst} 3/8\ S_8(g) + 2H_2O(g)$$

Uses of S, Se and Te

Most of the sulphur produced is used for the manufacture of sulphuric acid and other industrially important sulphur compounds. The most important application of Se is as a photoconductor in photocopying (Xerox) machines, though the major use is as a decolouriser of glass. Tellurium is mostly used as an additive in metallurgy (manufacture of iron and steel, non-ferrous metals and alloys). Tellurium and polonium are highly toxic, the latter more so because of its intense radioactivity.

Table 8.6 Atomic and Physical Properties of Group 16 Elements

Property	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic mass	16.00	32.06	78.96	127.60	210
Electronic configuration	$[He]2s^22p^4$	$[Ne]3s^23p^4$	$[Ar]3d^{10}4s^24p^4$	$[Kr]4d^{10}5s^25p^4$	$[Xe]4f^{14}5d^{10}6s^26p^4$
Covalent radius/pm	74	103	119	142	168
Ionic radius/pm (M^{-2})	140	184	198	221	230[a]
Ionisation enthalpy/(kJ mol^{-1}) I	1314	1000	941	869	813
II	3388	2251	2045	1790	–
Electronegativity	3.50	2.44	2.48	2.01	1.76
Density[b]	1.32[c]	2.06[d]	4.19[e]	6.25	–
Melting point/K	54	393[f]	490	725	520
Boiling point/K	90	718	958	1260	1235

[a] Approximate value; [b] g cm^{-3} at 298 K; [c] At the melting point; [d] Rhombic sulphur; [e] Hexagonal grey allotrope; [f] Monoclinic form, 673 K.

8.4.3 Allotropy of Sulphur and Selenium

Sulphur provides a very good example of an element that exhibits allotropy. It forms numerous allotropes of which the **yellow ortho-rhombic** and α- and β-**monoclinic** forms are the most important. The stable form at room temperature is ortho rhombic sulphur, which transforms to monoclinic sulphur when heated above 369-K. Both ortho rhombic and monoclinic sulphur are molecular solids; S_8 molecules are packed up to give different crystal structure for the two forms. The S_8 ring in both the forms is puckered and has a crown shape. The molecular dimensions are shown in [Fig. 8.9(a)].

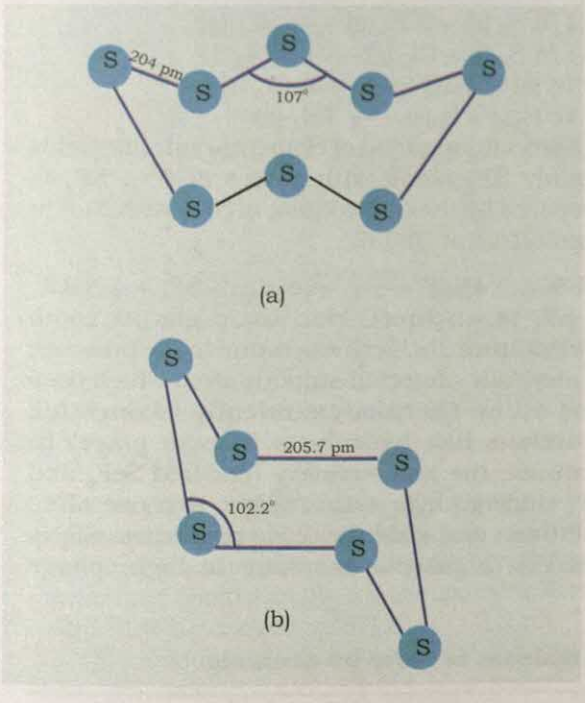


Fig. 8.9 *The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 allotrope.*

Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades. In cyclo-S_6, the ring adopts the chair form and the molecular dimensions are shown in fig. 8.9(b). In addition, various chain polymers called **catena-S_n** are known. Unstable small molecules, S_n (n = 2-5) exist in liquid sulphur at elevated temperatures and in sulphur vapour. At 1000 K, S_2 is the dominant species. Like dioxygen (O_2), S_2 is paramagnetic.

Selenium exists in eight allotropic forms of which three are **red monoclinic** forms containing Se_8 rings. The thermodynamically stable form is **grey hexagonal** 'metallic' selenium which consists of polymeric helical chains. The common form of the element is the amorphous black selenium. Grey selenium is the only allotrope of selenium which conducts electricity. Tellurium has only one crystalline form with a chain structure similar to that of grey Se.

Example 8.4
Why does sulphur in vapour state exhibit paramagnetic behaviour?

Solution
In vapour state sulphur partly exists as S_2 molecule and S_2 molecule like O_2 has two unpaired electrons in the antibonding π^* orbital and hence exhibits paramagnetism.

8.4.4 Oxidation States and Trends in Chemical Reactivity

The important oxidation states observed for S, Se and Te are –2, +2, +4 and +6 (Table 8.1). The chalcogenide dianions (E^{2-}) exist only in their compounds with the most electropositive elements. By and large, chalcogens with the exception of polonium, display non-metallic covalent chemistry. Some trends observed in the chemistry of group 16 elements may be summarised as follows:

(a) After oxygen, there is a steep drop in electronegativity for S, Se, Te and Po and consequently their compounds have less ionic character.

(b) The metallic character increases as we descend the group. Thus, sulphur is a typical non-metal and is an insulator; Se and Te are metalloids and are semi-conductors. Polonium shows metallic character.

(c) The thermal stability of the hydrides decreases in the order: $H_2O > H_2S > H_2Se > H_2Te > H_2Po$.

(d) The tendency for catenation decreases appreciably as we move down the group.

(e) Sulphur and other elements of the group can form compounds in which there are more than two covalent bonds to other elements. The oxidation states +4 and +6 are particularly important for sulphur and the heavier chalcogenides. Examples are SF_6, $SeCl_4$ and $Te(OH)_6$.

(f) The tendency to engage in multiple bonding decreases as we descend the group. Thus, S = C = S is moderately stable; Se = C = Se decomposes readily; Te = C = Te is unknown.

8.4.5 Hydrides

Group 16 elements form binary hydrides H_2X (X = O, S, Se, Te or Po). The thermal stability of these hydrides decreases from oxygen to polonium. Unlike H_2O, the other hydrides are unpleasant foul smelling poisonous gases. Some physical properties are listed in Table 8.7. The unique behaviour of H_2O is due to extensive intermolecular hydrogen bonding (Unit 11, Class XI).

Hydrides of S, Se and Te are prepared by the action of acids on metal sulphides, selenides and tellurides respectively. You are already familiar with the Kipps' apparatus used for the generation of H_2S in the laboratory by the action of dilute sulphuric acid on FeS.

$$FeS\ (s) + 2\ H_3O^+\ (aq) \longrightarrow Fe^{2+}\ (aq) + H_2S\ (g) + 2\ H_2O\ (l)$$

H_2S, H_2Se and H_2Te are weak diprotic acids in aqueous solutions; the acidity increases in the series $H_2S < H_2Se < H_2Te$.

Metal sulphides except those of groups 1 and 2 are sparingly soluble in water.

8.4.6 Halides

Sulphur and heavier chalcogens form a number of halides in their oxidation states +1, +2, +4 and +6. The well characterised chalcogen halides are:

Sulphur	*Se and Te*
S_2X_2 (X = F, Cl, Br or I)	Se_2Cl_2, Se_2Br_2 .
SX_2 (X = F or Cl)	$SeCl_2$, $TeCl_2$, $SeBr_2$, $TeBr_2$.
SF_4	SeX_4 , TeX_4 (X = F,Cl. or Br); TeI_4.
SF_6	SeF_6 , TeF_6.

The stability of the halides decreases in the order F>Cl>Br>I. The highest oxidation state is realised only in the fluorides. With iodine, only a tetraiodide, TeI_4 is known.

The general preparative routes for chalcogen halides involve the direct reaction of the chalcogen with the respective halogen. Some typical reactions are shown below:

$$1/8\ S_8\ (s) + 3\ F_2\ (g) \longrightarrow SF_6\ (g)$$

$$1/4\ S_8\ (l) + Cl_2\ (g) \longrightarrow S_2Cl_2\ (l)$$

$$Te\ (s) + 2\ Cl_2\ (g) \longrightarrow TeCl_4\ (s)$$

$$Te\ (s) + 2\ I_2\ (s) \longrightarrow TeI_4\ (s)$$

Direct fluorination of elemental sulphur yields mainly SF_6 along with traces of SF_4. SF_4 is prepared by the fluorination of SCl_2 with NaF in acetonitrile at 350 K.

$$3\ SCl_2 + 4NaF \xrightarrow{MeCN,\ 350\ K} S_2Cl_2 + SF_4 + 4\ NaCl$$

SF_6 is an inert, non-toxic gas at room temperature. Its inertness is due to the presence of sterically protected sulphur atom which does not allow thermodynamically favourable reactions like hydrolysis to take place. In contrast, the less sterically hindered SeF_6 and SF_4 undergo hydrolysis readily. Because of its inertness and good dielectric properties, SF_6 is used as a gaseous insulator in high voltage

Table 8.7 Some Physical Properties of Hydrides of Group 16 Elements

Property	H_2O	H_2S	H_2Se	H_2Te
Melting point in K	273	188	208	222
Boiling point in K	373	213	232	269
M-H distance in pm	96	134	146	169
HMH angle (°)	104	92	91	90
$\Delta_f H^\ominus$ in (kJ mol^{-1})	–286	– 20	– 73	– 100
E(M-H) in (kJ mol^{-1})	463	347	276	238
Dissociation constant[a]				
HM^- K_1	1.8×10^{-16}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}
M^{2-} K_2	–	7.1×10^{-15}	1.0×10^{-11}	1.6×10^{-11}

[a] aqueous solution, 298 K

generators. Both SF_4 and SeF_4 are used as fluorinating agents for conversion of -COOH into $-CF_3$ and C=O and P=O groups into CF_2 and PF_2 groups.

The structures of SF_4 and SF_6 are shown in Fig. 8.10. Compared to sulphur halides, the halides of Se and especially Te, in the +4 oxidation state, adopt oligomeric or polymeric structures. Thus, $SeCl_4$, $SeBr_4$, $TeCl_4$, $TeBr_4$ and TeI_4 exist as tetramers while TeF_4 has a polymeric structure.

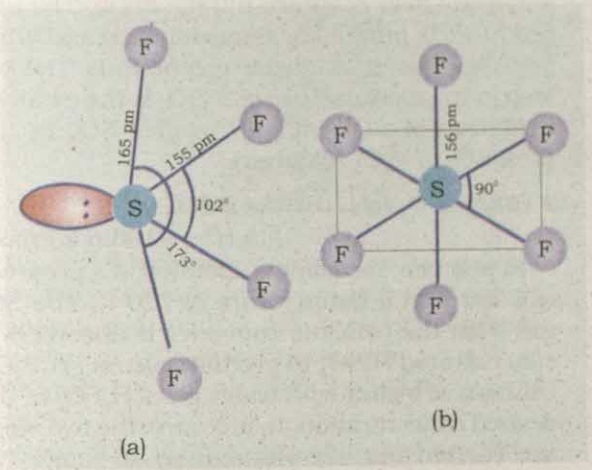


Fig. 8.10 *The structures of (a) SF_4 and (b) SF_6.*

8.4.7 Oxides

The principal oxides of group 16 elements have the general formula EO_2 and EO_3 (E = S, Se, or Te) of which the oxides of sulphur are the most important commercially for the manufacture of sulphuric acid (Section 8.4.8).

The dioxides result from the direct union of the elements:

$$S_8(s) + 8\ O_2(g) \longrightarrow 8\ SO_2\ (g)$$

SO_2 is a gas at room temperature and has an angular structure with a bond angle of 119° and S-O distance of 143 pm. It exists as discrete SO_2 molecules even in the solid state. SeO_2 in the gas phase has a structure similar to that of SO_2 but in the solid state has an infinite covalent chain structure (Fig. 8.11). TeO_2 in the solid state has a layer structure consisting of TeO_4 units.

SO_3 in the gas phase exists as planar triangular molecular species (Fig. 8.12).

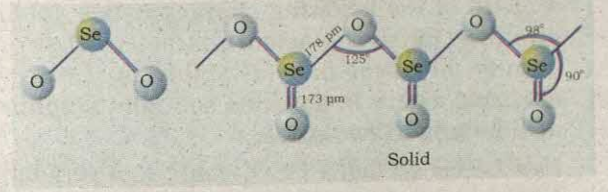


Fig. 8.11 *The structures of SeO_2 in the gas and solid phases.*

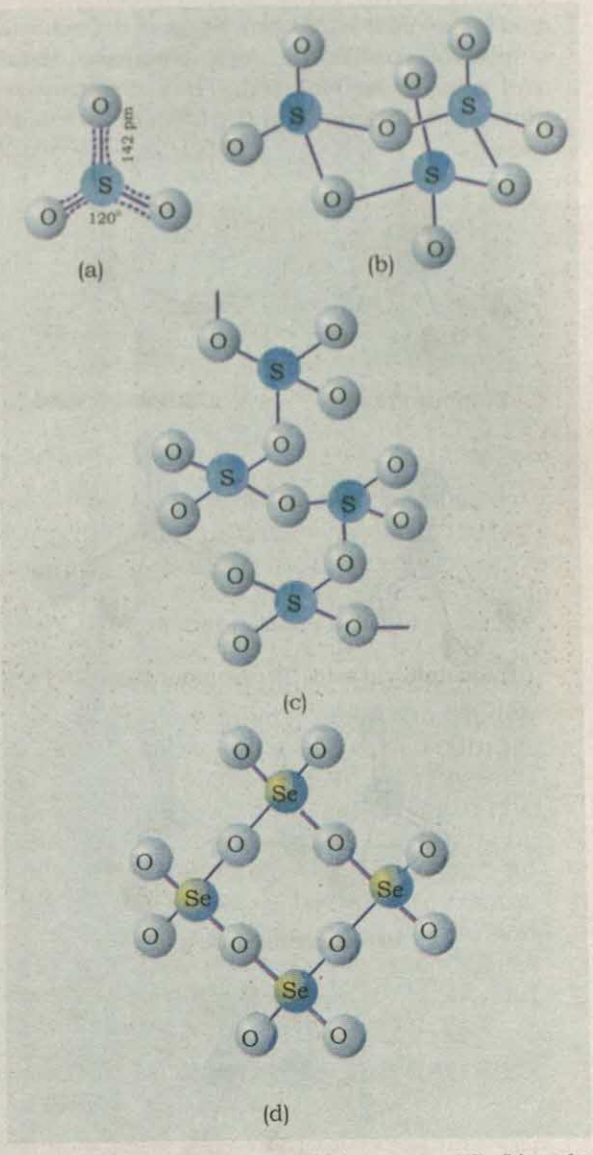


Fig. 8.12 *The structures of (a) gaseous SO_3 (b) cyclic trimer of solid SO_3 (c) linear chain form of solid SO_3 and (d) cyclic tetrameric form of SeO_3.*

In the solid state, SO_3 exists in several modifications having a linear cyclic trimeric or a polymeric chain structure as shown in Fig. 8.12. SeO_3, on the other hand, exists as a cyclic tetramer (Se_4O_{12}) in the solid state (Fig. 8.12).

TeO_3 is also a solid with a network structure in which TeO_6 octahedra share all vertices.

8.4.8 Oxoacids of Sulphur

Sulphur forms many oxoacids and the principal ones are shown in Fig. 8.13 of which sulphuric acid is the most important. Some of the acids (e.g. sulphurous or thiosulphuric acids) are unstable and cannot be isolated. They are known in aqueous solutions or in the form of their salts.

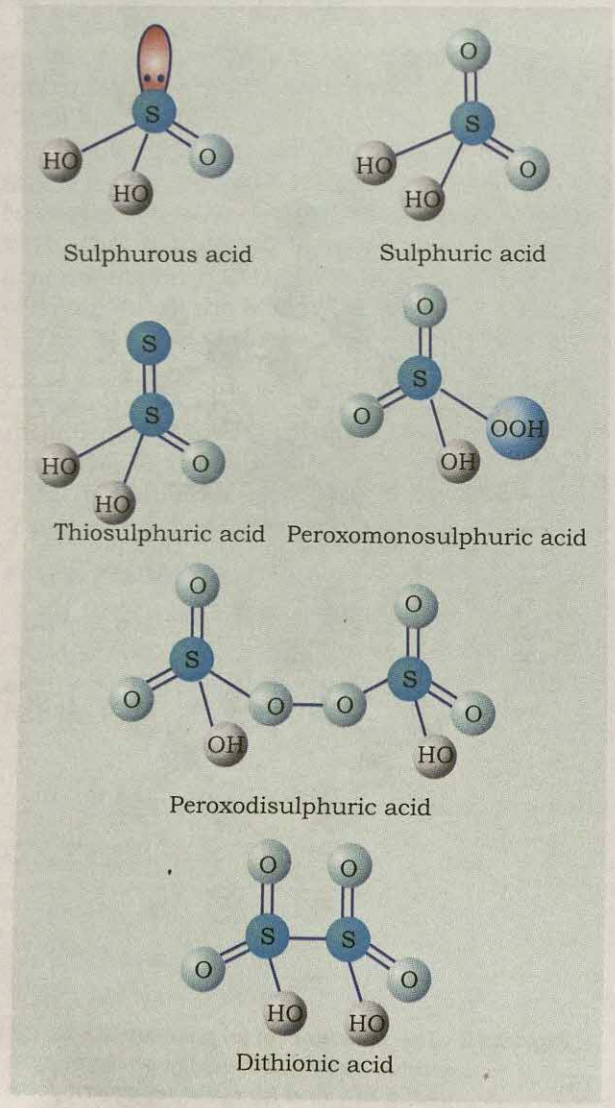


Fig. 8.13 *Some important oxo acids of sulphur.*

SULPHURIC ACID (H_2SO_4) is the most important industrial chemical produced worldwide. In this Section, we will deal with the manufacture, reactions and uses of sulphuric acid.

Manufacture of Sulphuric Acid

Sulphuric acid is manufactured by the **CONTACT PROCESS** which involves three stages :

(i) burning of sulphur or sulphide ores in air to generate SO_2.

(ii) conversion of SO_2 to SO_3 by reaction with oxygen in the presence of a catalyst, and

(iii) absorption of SO_3 in H_2SO_4 to give OLEUM which is formulated as $H_2S_2O_7$.

A flow diagram for the manufacture of sulphuric acid is shown in (Fig. 8.14). The SO_2 produced is purified by removing dust and other impurities such as arsenic compounds. The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).

$$2\ SO_2(g) + O_2\ (g) \xrightarrow{V_2O_5} 2\ SO_3\ (g)$$

$$\Delta_r H^\ominus = -196.6\ kJ\ mol^{-1}$$

In practice, the plant is operated at a pressure of 2 bar and a temperature of 720 K. The SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce 'oleum', $H_2S_2O_7$. Dilution of oleum with water gives H_2SO_4 of the desired concentration. In industry, the two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \longrightarrow 2\ H_2SO_4$$

The sulphuric acid obtained by the contact process is generally of 96-98% purity.

Properties and Reactions of Sulphuric Acid

Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 g cm^{-3} at 298 K. The acid freezes at 283 K and boils at 590 K. It dissolves in water with the evolution of a large quantity of heat. Hence, care must be taken while preparing sulphuric acid solution from concentrated sulphuric acid. The concentrated acid must be added slowly into water with constant stirring.

The chemical reactions of sulphuric acid are a result of the following characteristics: (a) low volatility, (b) strong acidic character, (c) strong affinity for water and (d) ability to act as an oxidizing agent. In aqueous solution, sulphuric acid ionizes in two steps:

$H_2SO_4 \longrightarrow H^+\ (aq) + HSO_4^-\ (aq)$; K_1 = very large

$HSO_4^-\ (aq) \longrightarrow H^+(aq) + SO_4^{2-}\ (aq)$;

$K_2 = 1.2 \times 10^{-2}$

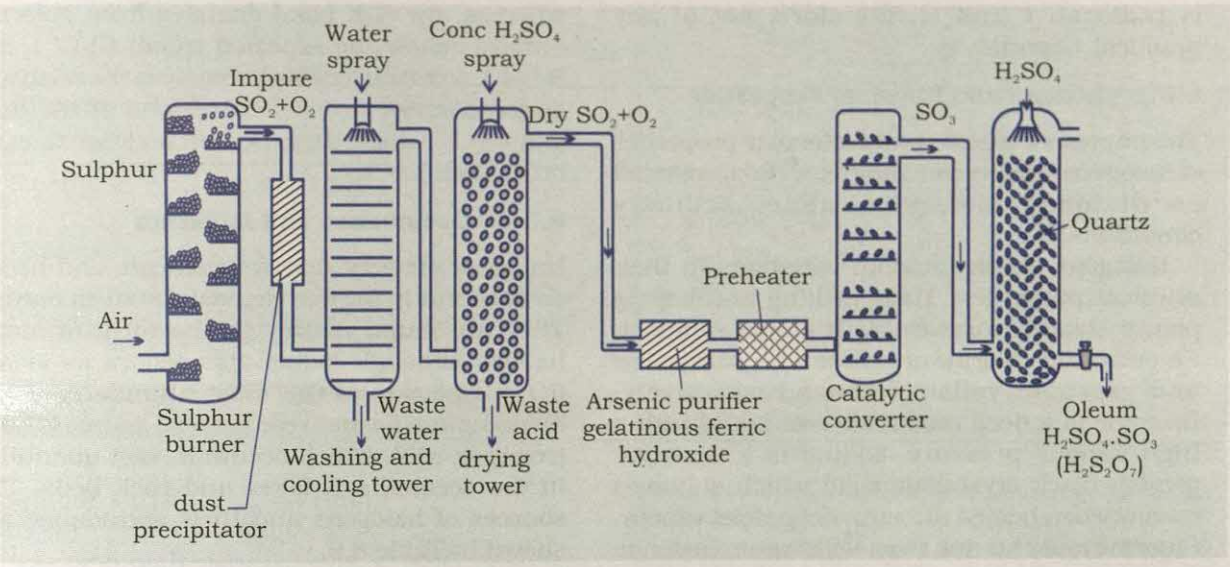


Fig. 8.14 *Flow diagram for the manufacture of sulphuric acid.*

The acid forms two series of salts; normal sulphates (such as sodium sulphate and copper sulphate) and acid sulphates (e.g., sodium bisulphate). The sulphate ion, SO_4^{2-} is tetrahedral with an S-O bond length of 149 pm.

Sulphuric acid, because of its low volatility, can be used to manufacture more volatile acids from their corresponding salts:

$$2\ MX + H_2SO_4 \longrightarrow 2\ HX + M_2SO_4$$
$$(X = F^-, Cl^-, NO_3^-)$$

Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing these through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compounds as shown by its charring action on carbohydrates.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12\ C + 11\ H_2O$$

Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2.

$$C + 2\ H_2SO_4 \longrightarrow CO_2 + 2\ SO_2 + 2\ H_2O$$

$$Cu + 2\ H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2\ H_2O$$

With zinc, which is a stronger reducing agent than copper, the reduction of concentrated sulphuric acid goes further to give sulphur or H_2S.

Uses

Sulphuric acid is a prime industrial chemical. A nation's industrial strength can be gauged by the quantity of sulphuric acid it produces and consumes. It is needed for the manufacture of hundreds of other compounds and also in many industrial processes. The bulk of sulphuric acid produced is used in the manufacture of fertilizers (e.g., ammonium sulphate, superphosphate). Other uses are in (a) petroleum refining, (b) manufacture of pigments, paints and dyestuff intermediates, (c) detergent industry, (d) metallurgical applications (e.g., cleansing metals before enameling, electroplating and galvanising), and (e) storage batteries. Currently, our country produces more than 2.5 million tonns of sulphuric acid per annum compared to over 40 million tonns produced in U.S.A. and 120 million tonns produced worldwide.

8.5 GROUP 17 ELEMENTS: THE HALOGEN FAMILY

Group 17 of the Periodic table contains the elements-fluorine, chlorine, bromine, iodine and astatine. These elements are collectively known as the **HALOGENS**. This name is derived from two Greek words Halo and Gens meaning '**salt producing**'. Halogens are among the most reactive non-metals. There are greater similarities within the halogen group compared to other groups in the Periodic table with the exception of the alkali metals (group 1). Astatine

is radioactive and is, therefore, not of any practical importance.

8.5.1 Atomic and Physical Properties

The important atomic and molecular properties of halogens are given in Table 8.8. Halogens exist as diatomic molecules under ordinary conditions.

Halogens display smooth variations in their physical properties. Their melting and boiling points steadily increase with atomic number. Fluorine and chlorine are gases with pale yellow and greenish yellow colours respectively. Bromine is a deep reddish-brown liquid with a high vapour pressure. Iodine is a lustrous greyish black crystalline solid which sublimes readily when heated to form a deep violet vapour. Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.

One curious anomaly we note from Table 8.8 is the smaller enthalpy of dissociation of F_2 compared to that of Cl_2. In other words, the F-F bond energy is smaller than that of Cl-Cl whereas, the X-X bond energies from chlorine onwards show the expected trend: Cl-Cl > Br-Br > I-I. A reason for this anomaly is the relatively larger electron-electron repulsions of the lone pairs in F_2 where they are much closer to each other than in Cl_2.

8.5.2 Occurrence and Isolation

Halogens are very reactive elements and hence do not occur in the free elemental state in nature. They are found mainly in the form of metal halides although iodine also occurs as iodate (IO_3^-). Chlorine is the most abundant of the halogens and its main commercial source is NaCl (common salt), which occurs in vast quantities in the oceans, salt lakes and rock beds. The sources of halogens and their abundance are shown in Table 8.9.

Because fluorine is the strongest chemical oxidizing agent, the only practicable method of preparing elemental fluorine is by an electrolytic method developed by Moissan in 1886. Electrolysis of a molten mixture of potassium fluoride and anhydrous hydrogen fluoride at ~350 K using mild steel and carbon rod free from graphite as cathodes and anodes respectively gives elemental fluorine :

Table 8.8 Atomic and Molecular Properties of Halogens

Property	F	Cl	Br	I	At[a]
Atomic number	9	17	35	53	85
Atomic mass	19.00	35.45	79.90	126.90	210
Electronic configuration	[He]$2s^2 2p^5$	[Ne]$3s^2 3p^5$	[Ar]$3d^{10} 4s^2 4p^5$	[Kr]$4d^{10} 5s^2 5p^5$	[Xe]$4f^{14} 5d^{10} 6s^2 6p^5$
Covalent radius in pm	64	99	114	133	–
Ionic radius X^- in pm	133	184	196	220	–
Ionization enthalpy in (kJ mol^{-1})	1680	1256	1142	1008	–
Electron gain enthalpy in (kJ mol^{-1})	-333	-349	-325	-296	–
Electronegativity[b]	4	3.2	3.0	2.7	2.2
	F_2	Cl_2	Br_2	I_2	
Melting point in K	54.4	172.0	265.8	386.6	–
Boiling point in K	84.9	239.0	332.5	458.2	–
Density in g cm^{-3}	1.51(85)[c]	1.66(203)[c]	3.19(273)[c]	4.94(293)[d]	–
Distance X–X in pm	143	199	228	266	–
Enthalpy of dissociation $X_2(g) \longrightarrow 2X(g)$ in (kJ mol^{-1})	158.8	242.6	192.8	151.1	–
$E^\ominus$ / V[e]	2.87	1.36	1.09	0.54	–

[a] Radioactive; [b] Pauling scale; [c] For the liquid at temperatures (K) given in the parentheses; [d] solid; [e] The half-cell reaction is $X_2(aq) + 2e^- \longrightarrow 2X^-(aq)$.

Table 8.9

Halogen	Abundance		Main sources
	Crustal rocks	Oceans	
Fluorine	5.44×10^{-2}	7.0×10^{-6}	Fluorite (CaF_2), Fluorapatite [$Ca_5(PO_4)_3F$], Cryolite (Na_3AlF_6)
Chlorine	1.26×10^{-2}	1.9	Sea water, salt wells, salt beds (NaCl, KCl, $MgCl_2$, $CaCl_2$)
Bromine	0.25×10^{-3}	6.5×10^{-3}	Sea water, salt lakes (NaBr, KBr, $MgBr_2$)
Iodine	4.6×10^{-5}	5.0×10^{-6}	Brine wells, sea weeds (I^-), Chile salt petre ($NaIO_3$)

Cathode : $2H^+ + 2e^- \longrightarrow H_2(g)$

Anode : $2F^- \longrightarrow F_2(g) + 2e^-$

A diaphragm made of teflon is used to separate the cathode and the anode to avoid the accidental explosive mixing of hydrogen and fluorine.

Chlorine is produced industrially by the electrolysis of natural brine or aqueous solutions of NaCl. Sodium hydroxide and hydrogen are also produced in this method (Unit 12, Class XI). In the laboratory, chlorine can be prepared by the oxidation of HCl by MnO_2 or by $KMnO_4$.

$$MnO_2(s) + 4\ HCl\ (aq) \rightarrow MnCl_2\ (aq) + 2\ H_2O(l) + Cl_2(g)$$

$$2KMnO_4(s) + 16\,HCl(aq) \rightarrow 2KCl(aq) + 2MnCl_2(aq) + 8H_2O(l) + 5\ Cl_2(g)$$

Bromine is commercially produced by the oxidation of bromide ions in natural brine with chlorine:

$$2\ Br^-\ (aq) + Cl_2\ (g) \longrightarrow Br_2(l) + 2\ Cl^-\ (aq)$$

Similarly, iodine is manufactured from natural brines or sea weed by the oxidation of iodide ion with chlorine. Iodine is recovered from iodates (occurring in Chile salt petre) by reduction with sodium hydrogen sulphite, $NaHSO_3$ by the sequence of reactions:

$$NaIO_3\,(aq) + 3\ NaHSO_3\ (aq) \longrightarrow NaI\ (aq) + 3\ NaHSO_4\ (aq)$$

$$NaIO_3\,(aq) + 5\ NaI\ (aq) + 3\ H_2SO_4\ (aq) \longrightarrow 3\ I_2\ (s) + 3\ H_2O(l) + 3\ Na_2SO_4\ (aq)$$

Example 8.5

Chlorine vapours are evolved when concentrated sulphuric acid is added to a mixture of sodium chloride and manganese dioxide. Write a balanced equation for the reaction.

Solution

$$2\ NaCl\ (s) + 2\ H_2SO_4(aq) + MnO_2(s) \longrightarrow Na_2SO_4(aq) + MnSO_4(aq) + 2\ H_2O(l) + Cl_2(g)$$

8.5.3 Oxidation States and Trends in Chemical Reactivity

The molecular structures of halogens are similar. All are diatomic and many properties change uniformly down the group. All the halogens are reactive non-metals. Since fluorine is the most electronegative element, it has an oxidation state of –1 in all its compounds.

The ready acceptance of an electron is the reason for the strong oxidizing nature of halogens. F_2 is the strongest oxidizing halogen and it oxidizes other halide ions in solution or even in the solid phase. In general, a halogen oxidizes halide ions of higher atomic number halogens as illustrated belows:

$$F_2 + 2\ X^- \longrightarrow 2\ F^- + X_2\ (X = Cl, Br \text{ or } I)$$

$$Cl_2 + 2\ X^- \longrightarrow 2Cl^- + X_2\ (X = Br \text{ or } I)$$

$$Br_2 + 2\ I^- \longrightarrow 2\ Br^- + I_2$$

Chemical method for the preparation of fluorine

Recently, a chemical method for the preparation of fluorine has been developed. This involves the following reaction:

$$K_2MnF_6 + 2\ SbF_5 \longrightarrow 2\ KSbF_6 + MnF_3 + \tfrac{1}{2}\ F_2$$

In this reaction, the stronger Lewis acid SbF_5 displaces the weaker one, MnF_4 from its salt. MnF_4 is unstable and readily decomposes to give MnF_3 and fluorine.

The decreasing oxidising ability of the halogens as we go down the group is reflected in their standard reduction potentials E° (Table 8.8).

Halogens combine directly with most metals and several non-metals to give halides. The reactivity decreases in the order $F_2 > Cl_2 > Br_2 > I_2$. Fluorine forms compounds with all other elements under appropriate conditions except helium, argon and neon. Some examples of the reactions of halogens with metals and non-metals are shown below:

$Mg\ (s) + Br_2\ (l) \longrightarrow MgBr_2\ (s)$

$Xe\ (g) + 3\ F_2\ (g) \longrightarrow XeF_6\ (g)$

$\frac{1}{2}\ P_4\ (s) + 3\ Cl_2\ (g) \longrightarrow 2PCl_3\ (l)$

$1/8\ S_8\ (s) + 3\ F_2\ (g) \longrightarrow SF_6\ (g)$

The ionic character of the M-X bond decreases in the order M-F > M-Cl > M-Br > M-I. If a metal exhibits more than one oxidation state, the halide in the higher oxidation state will be more covalent than the one in lower oxidation state. For example, $SnCl_4$, $PbCl_4$, $SbCl_5$, UF_6 are more covalent than $SnCl_2$, $PbCl_2$, $SbCl_3$ and UF_4, respectively.

Halogens also combine among themselves to form a number of **INTERHALOGEN COMPOUNDS**, XX'_n (Section 8.5.7).

8.5.4 Hydrogen Halides

Halogens combine with hydrogen to form covalent molecular species HX known as hydrogen halides. Aqueous solutions of the hydrogen halides are known as hydrohalic acids. Among these, hydrochloric acid is a major industrial chemical; world production is of the order of 10 million tonnes per annum.

Hydrogen fluoride and hydrogen chloride are commercially manufactured respectively by heating, i) a mixture of calcium fluoride (fluorite or fluorospar) and ii) sodium chloride with concentrated sulphuric acid.

$$CaF_2(s) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + 2HF(g)$$

$$2NaCl(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(s) + 2HCl(g)$$

In recent years, chemical industry producing chloro-organics has emerged as the major commercial source of HCl as a by-product.

Commercially, HBr is prepared by the direct reaction of H_2 and Br_2 at ~ 570 K in the presence of a Pt catalyst. HI is produced by the reaction of I_2 with H_2S or hydrazine.

$$H_2(g) + Br_2\ (g) \xrightarrow{\text{Pt / asbestos}} 2\ HBr$$

$$2\ I_2(s) + N_2H_4\ (aq) \xrightarrow{573\ K} 4\ HI\ (aq) + N_2\ (g)$$

Treatment of metal bromides or iodides with conc. H_2SO_4 is not satisfactory for the preparation of HBr and HI because the HBr or HI formed are oxidised by H_2SO_4 and the product is contaminated with the respective halogen. This difficulty can be overcome by using a non-oxidizing acid such as H_3PO_4.

Example 8.6

Suggest a method for the laboratory preparation of DCl. Write a balanced equation for the reaction.

Solution

PCl_5 may be hydrolysed with heavy water (D_2O) to give DCl.

$$PCl_5 + D_2O \longrightarrow POCl_3 + 2DCl$$

Hydrogen halides are colourless irritating gases at room temperature. Their boiling and melting points show a regular gradation from HCl to HI. The boiling and melting points of HF are abnormally high because of hydrogen bonding.

HCl , HBr , and HI are all very strong acids in aqueous solution and their acidity increases in the order HCl < HBr < HI. In contrast, HF is a much weaker acid as shown by the pK_a values (Table 8.10). This is attributed to the strong

Table 8.10 Properties of Hydrogen Halides

Property	HF	HCl	HBr	HI
Melting point in K	190	159	185	222
Boiling point in K	293	189	206	238
Bond length (H-X) in pm	91.7	127.4	141.4	160.9
Dipole moment μ in D	1.86	1.11	0.79	0.38
$\Delta_{diss.}H^\ominus$ in (kJ mol^{-1})	574	432	363	295
Acid dissoc. const. pK_a	3.2	–7.0	–9.5	–10.0

hydrogen bonding of F^- to H_3O^+ compared to the other halide ions. Hydrohalic acids, in particular HF, are corrosive and extreme care has to be taken while working with them. Hydrofluoric acid attacks glass and hence it is used for etching glass and manufacture of glass shell of television tubes.

8.5.5 Oxides

Halogens form many binary compounds with oxygen but most of them are unstable. Fluorine forms two binary compounds with oxygen, OF_2 and O_2F_2, which are properly called oxygen fluorides because of the higher electronegativity of fluorine. Both are strong fluorinating agents. O_2F_2 oxidises plutonium to PuF_6 and this reaction is used in removing plutonium as PuF_6 from spent nuclear fuel. Chlorine, bromine and iodine form oxides in which the oxidation state of halogen varies from +1 to +7. Of these, the most important are Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7. Chlorine dioxide is the only one prepared on a large scale by the reduction of ClO_3^- with SO_2 in a strongly acidic solution:

$$2\ NaClO_3\,(aq) + SO_2\,(g) \xrightarrow{acid} 2\ ClO_2\,(g) + Na_2SO_4(aq)$$

The chlorine oxides are powerful oxidizing agents and decompose explosively when subjected to mechanical shock or on heating. Despite these hazards, ClO_2 is used as a bleaching agent for paper pulp and textiles and to disinfect sewage and drinking water.

8.5.6 Oxoacids

In line with its high electronegativity and small size, fluorine forms only one oxoacid HOF known as fluoric(I) acid or hypofluorous acid. The other halogens form several oxoacids. Most of them cannot be isolated pure. They are stable only in aqueous solutions or in the form of their salts. The oxoacids of halogens are shown below.

The strength of halic acids increases appreciably with increase in the oxidation state of the halogens: pK_a for HOCl, $HOClO$, $HOClO_2$ and $HOClO_3$ are 7.5, 2.0, −1.2 and −10 respectively. The strength of halic acids with the same oxidation state of the halogens, decreases in the sequence I > Br > Cl. Among the oxoacids of the halogens, those of chlorine are the most important and are discussed in some detail in this section.

Chloric(I) acid, HOCl is formed by the disproportionation of chlorine in water:

$$Cl_2\,(g) + H_2O\,(l) \longrightarrow HOCl\,(aq) + HCl\,(aq)$$

Pure HOCl can be prepared by the addition of HgO or Ag_2O to chlorine water:

$$2\ Cl_2 + 2\ HgO + H_2O \longrightarrow HgO.HgCl_2 + 2\ HOCl$$

Chloric (I) acid is stable only in solution. The oxoanion is **ClO^-**, **hypochlorite** or **[monoxochlorate(I)]**. NaOCl is used as household bleach and is commercially produced by the electrolysis of cold dilute NaCl solution under conditions where chlorine liberated reacts with the hydroxide ion to produce the hypochlorite ion:

$$Cl_2\,(g) + 2\ OH^-\,(aq) \longrightarrow Cl^-\,(aq) + OCl^-\,(aq) + H_2O(l)$$

Powdered calcium halate(I), $Ca(OCl)_2.2H_2O$ is used for disinfecting swimming pool water. For general bleaching and sanitation purposes, **bleaching powder**, produced by passing chlorine over slaked lime and having the composition $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$, is used. Halate(I) salts react with acids to liberate chlorine, for example:

$$Ca(OCl)_2(s) + 4\ HCl(aq) \longrightarrow CaCl_2\,(aq) + 2H_2O(l) + 2\ Cl_2(g)$$

Chloric(III) acid, HOClO is prepared by the reaction of $Ba(ClO_2)_2$ (formed by the treatment of $Ba(OH)_2$ with H_2O_2 and ClO_2) with dilute sulphuric acid.

Halic (I) acid (Hypohalous acid)	HOF (hypofluorous acid)	HOCl (hypochlorous acid)	HOBr (hypobromous acid)	HOI (hypoiodous acid)
Halic (III) acid (Halous acid)	–	HOClO (chlorous acid)	–	–
Halic (V) acid (Halic acid)	–	$HOClO_2$ (chloric acid)	$HOBrO_2$ (bromic acid)	$HOIO_2$ (iodic acid)
Halic (VII) acid (Perhalic acid)	–	$HOClO_3$ (perchloric acid)	$HOBrO_3$ (perbromic acid)	$HOIO_3$ (periodic acid)

$$Ba(OH)_2 + H_2O_2 + 2ClO_2 \longrightarrow Ba(ClO_2)_2 + 2H_2O + O_2$$

$$Ba(ClO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow + 2\ HOClO$$

Among the salts of chloric(III) acid, $NaClO_2$ is commercially important as a bleaching agent for textiles and for removal of $(NO)_x$ pollutants from industrial waste gases.

Chloric(V) acid, $HOClO_2$ is stable only in solution. When chlorine is passed through hot concentrated alkali solutions, [trioxochlorate(V)] salts are formed:

$$6\ Cl_2\ (g) + 6\ Ba(OH)_2(aq) \longrightarrow Ba(ClO_3)_2\ (aq) + 5\ BaCl_2\ (aq) + 6H_2O\ (l)$$

The free acid is obtained by treating the barium salt with dilute H_2SO_4:

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow 2\ HClO_3 + BaSO_4$$

[Tetraoxochloric(VII)] or perchloric acid, $HClO_4$ is obtained by treating anhydrous $NaClO_4$ or $Ba(ClO_4)_2$ with concentrated HCl:

$$NaClO_4 + HCl \longrightarrow NaCl\ (s) + HClO_4\ (aq)$$

The free acid $HClO_4$ explodes above 365 K but it can be distilled at low temperatures under reduced pressure. Commercially $NaClO_4$ is made by the electrolytic oxidation of $NaClO_3$. An important chlorate(VII) salt is ammonium perchlorate, NH_4ClO_4 which is used as an oxidizer in solid rocket propellants in missile and space programmes (Unit 18). It is produced from $NaClO_4$ by the reaction:

$$NaClO_4\ (aq) + NH_4Cl\ (aq) \longrightarrow NaCl\ (aq) + NH_4ClO_4\ (s)$$

Ammonium perchlorate is less soluble than sodium perchlorate and is precipitated as a solid.

Sodium chlorate $NaClO_3$ is produced on a large scale by the electrolysis of brine in a cell where efficient mixing of chlorine produced at the anode with the OH^- produced at the cathode takes place.

Sodium chlorate is the precursor for the production of ClO_2 used for bleaching paper pulp. You must have seen dazzling fireworks and flares during Diwali or other festival times. These fireworks contain $KClO_3$ as the oxidiser and the various colours are obtained by adding small quantities of Sr(red), Ba(green) or Cu(blue) salts. $KClO_3$ is also used in the head of safety matches.

The structures of the oxoacids of chlorine are shown in Fig. 8.15.

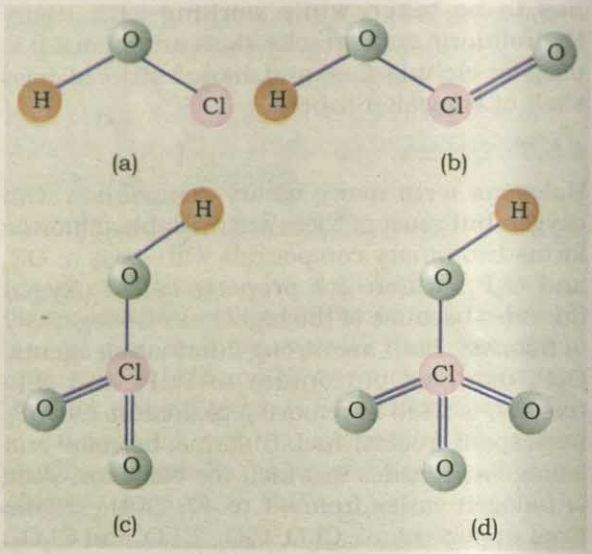


Fig. 8.15 *The structures of (a) chloric(I) acid (b) chloric(III) acid (c) chloric(V) acid and (d) chloric(VII) acid.*

8.5.7 Interhalogen Compounds

Halogens react with each other to produce a number of **INTERHALOGEN COMPOUNDS** XX'_n where n = 1,3,5 or 7. Some of the interhalogen compounds are shown below :

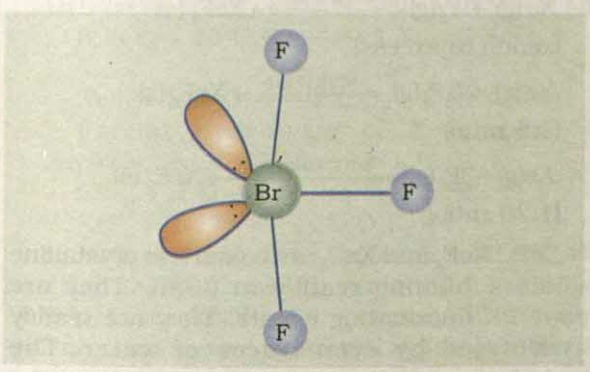
XX'	XX'_3	XX'_5	XX'_7
ClF	ClF_3	ClF_5	IF_7
BrF	BrF_3	BrF_5	
BrCl	IF_3	IF_5	
ICl	$ICl_3\ (I_2Cl_6)$		
IBr			
IF			

The stability of the interhalogen compounds increases as the size of the central atom increases. In these compounds, the smaller and the more electronegative atom is assigned a negative oxidation state. The interhalogen compounds are strong oxidising agents. They are essentially covalent. Their molecular structures are very interesting and can be explained on the basis of VSEPR theory. The XX'_3 compounds have the bent 'T' structure (Example 8.7). The XX'_5 compounds have the square pyramidal structure. IF_7 has the pentagonal bipyramidal structure. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of uranium (U^{235}).

$$U(s) + 3ClF_3(l) \longrightarrow UF_6(g) + 3ClF(g)$$

Example 8.7
Deduce the molecular shape of BrF_3 on the basis of VSEPR theory.

Solution
The central atom Br has seven electrons in the valence shell. Three of these will form electron-pair bonds with three fluorine atoms leaving behind four electrons. Thus, there are three bond pairs and 2 lone pairs. According to VSEPR theory, these will occupy the corners of a trigonal bipyramid. The two lone pairs will occupy the equatorial positions to minimize lone pair-lone pair and the bond pair-lone pair repulsions which are greater than the bond pair-bond pair repulsions. In addition, the axial fluorine atoms will be bent towards the equatorial fluorine in order to minimise the lone-pair-lone pair repulsions. The shape would be that of a slightly bent 'T'.



In addition to neutral interhalogen species, several polyhalide anions XY_{2n}^- (n = 1,2,3,4) and polyhalonium cations XY_{2n}^+ are known. The most important of these compounds is the linear triatomic iodide ion I_3^- which is formed when iodine dissolves in an aqueous solution of potassium iodide.

$$I_2\,(s) + I^-\,(aq) \longrightarrow I_3^-\,(aq)$$

Some of the important polyhalonium cations are ClF_2^+, Cl_2F^+, BrF_2^+, IF_2^+ and ICl_2^+.

8.5.8 Uses of Halogens and their Compounds

Fluorine is used mainly for the manufacture of UF_6 for nuclear power generation and SF_6 for dielectrics. The important organic chemicals derived from HF are the chlorofluorocarbons and polytetrafluoro-ethylene (TEFLON). Chlorofluorocarbons known as FREONS are used as refrigerants (these are, however, being phased out in favour of chlorofluoro hydrocarbons) and in aerosols and artificial blood. Minor uses of HF are in the glass industry as an etching agent and in the manufacture of fluoride salts. Prominent among the fluorides is NaF used for the fluoridation of water; one part per million level of fluoride in drinking water prevents tooth decay. SnF_2 is used in fluoride tooth pastes. Chlorine is used for the bleaching of paper, pulp and textiles and as disinfectant (Unit 18) for sterilising drinking water and in the production of organic compounds (e.g., polyvinyl chloride, chlorinated hydrocarbons, pharmaceuticals, herbicides, pesticides) and inorganic compounds (e.g., HCl, PCl_3 and NaOCl).

The main outlet for bromine is ethylene bromide which is used as a gasoline additive. Bromine is also used to make AgBr for photography. Iodine is used for the preparation of iodoform and potassium iodide. Iodide is necessary for the normal functioning of the thyroid gland. Insufficient iodine in the diet leads to **GOITRE** (enlargement of the thyroid gland). Hence, sodium or potassium iodate/iodide is added to table salt and this type of salt is known as **'iodised'** salt.

Example 8.8
With what neutral molecule is ClO^- isoelectronic?

Solution
ClF is isoelectronic with ClO^-.

8.6 GROUP 18 ELEMENTS : NOBLE GASES

Group 18 of the Periodic table consists of six elements – helium, neon, argon, krypton, xenon and radon which are collectively known as the **NOBLE GASES**.

8.6.1 Atomic and Physical Properties

The noble gases appear at the end of each period and have fully occupied orbitals in their valence shell ($1s^2$ for helium and ns^2np^6 for the other elements). Gain or loss of electrons requires high energies and hence these elements exhibit low chemical reactivity. Their physical properties show a smooth gradation and some important properties are listed in Table 8.11.

All the noble gases are monoatomic. They are colourless, odourless and tasteless. They are sparingly soluble in water. They have very low melting and boiling points because the only type of interatomic attraction in these elements is due to the weak dispersion interactions. Helium has the lowest boiling point of any known substance. It has the unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

8.6.2 Occurrence and Isolation of Noble Gases

All the noble gases except radon occur in the atmosphere. Their total abundance in dry air is ~ 1% by volume of which argon is the major component. Neon, argon, krypton and xenon are obtained as by-products of liquefaction of air and separation of its constituents by fractional distillation. The main commercial source of helium is natural gas. Helium is the second most abundant element in the universe (23% compared to 76% hydrogen) although its terrestrial abundance is very low. Radon is obtained as the decay product of ^{226}Ra.

$$^{226}_{88}Ra \rightarrow ^{222}_{86}Rn + ^{4}_{2}He$$

8.6.3 Chemistry of the Noble Gases

Noble gas compounds proved elusive for many years. The real chemistry of noble gases began in 1962 with the isolation of an orange yellow solid by Neil Bartlett from the reaction of xenon with PtF_6. Bartlett had noticed that PtF_6 reacts with oxygen to form $O_2^+[PtF_6]^-$ and since the ionization enthalpies of O_2 and Xe are close to each other (Xe 1170; O_2 1175 kJ mol^{-1}), he reasoned that PtF_6 would react with xenon to form $Xe^+[PtF_6]^-$*. Since this exciting discovery, several other xenon compounds, mainly with the most electronegative elements-fluorine and oxygen, have been synthesised. The compounds of krypton are fewer; only the difluoride (KrF_2) has been studied in detail. Compounds of radon have not been isolated but only identified by radiotracer techniques. No true compounds of Ar, Ne or He are known.

Xenon-fluoride compounds

Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6 by the direct union of elements under appropriate experimental conditions. XeF_2 can also be prepared by irradiating a mixture of xenon and fluorine with sunlight or light from a high pressure mercury arc lamp:

$$Xe(g) + F_2(g) \xrightarrow{673\,K,\ 1\ bar} XeF_2(s)$$

(xenon in excess)

$$Xe(g) + 2F_2(g) \xrightarrow{873\,K,\ 7\ bar} XeF_4(s)$$

(1:5 ratio)

$$Xe(g) + 3F_2(g) \xrightarrow{573\,K,\ 60\text{–}70\ bar} XeF_6(s)$$

(1:20 ratio)

XeF_2, XeF_4 and XeF_6 are colourless crystalline solids subliming readily at 298K. They are powerful fluorinating agents. They are readily hydrolysed by even traces of water. The hydrolysis of XeF_2 can be represented by the equation:

Table 8.11 Atomic and Physical Properties of Group 18 Elements (Noble Gases)

Property	He	Ne	Ar	Kr	Xe	Rn[a]
Atomic number	2	10	18	36	54	86
Atomic mass	4.00	20.18	39.10	83.80	131.30	222
Electronic configuration	$1s^2$	$[He]2s^22p^6$	$[Ne]3s^23p^6$	$[Ar]3d^{10}4s^24p^6$	$[Kr]4d^{10}5s^25p^6$	$[Xe]4f^{14}5d^{10}6s^26p^6$
Atomic radius (pm)	120	160	190	200	220	–
Ionisation enthalpy (kJ mol^{-1})	2372	2080	1520	1351	1170	1037
Density (at STP)/g cm^{-3}	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}	9.7×10^{-3}
Melting point/K	-	24.6	83.8	115.9	161.3	202
Boiling point/K	4.2	27.1	87.2	119.7	165.0	211
Atmospheric content (% by volume)	5.24×10^{-4}	1.82×10^{-3}	0.934	1.14×10^{-4}	8.7×10^{-6}	–

[a] radioactive

* *Recent studies indicate that this compound is to be formulated as* $[XeF]^+[Pt_2F_{11}]^-$.

$$2\,XeF_2\,(s) + 2\,H_2O(l) \longrightarrow 2Xe(g) + 4\,HF(aq) + O_2(g)$$

The structures of the three xenon fluorides can be deduced from VSEPR and these are shown in Fig. 8.16. XeF_2 and XeF_4 have the linear and square planar structures, respectively. XeF_6 has seven electron pairs (6 bonding pairs and one lone pair) and would thus have a distorted octahedral structure as found experimentally in the gas phase. In the solid state, XeF_6 contains tetrameric and hexameric units in which square pyramidal XeF_5^+ units are linked by bent F^- pyramidal bridges. Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.

$$XeF_2 + PF_5 \longrightarrow [XeF]^+\,[PF_6]^-$$
$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+\,[SbF_6]^-$$
$$XeF_6 + MF \longrightarrow M^+\,[XeF_7]^- \quad (M = Na, K, Rb \text{ or } Cs)$$

Xenon-oxygen compounds

Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3:

$$6\,XeF_4 + 12\,H_2O \longrightarrow 4\,Xe + 2\,XeO_3 + 24\,HF + 3\,O_2$$
$$XeF_6 + 3\,H_2O \longrightarrow XeO_3 + 6\,HF$$

Partial hydrolysis of XeF_6 gives the oxyfluorides $XeOF_4$ and XeO_2F_2.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2\,HF$$
$$XeF_6 + 2\,H_2O \longrightarrow XeO_2F_2 + 4\,HF$$

XeO_3 is a colourless explosive solid and has a trigonal pyramidal molecular structure (Fig. 8.16). $XeOF_4$ is a colourless volatile liquid and has a square pyramidal molecular structure (Fig. 8.16).

XeO_3 reacts with aqueous alkali to form the hydrogen xenate ion, $HXeO_4^-$, which slowly disproportionates to give xenon and perxenate ion XeO_6^{4-} in which xenon has the oxidation state +8.

$$XeO_3 + OH^- \longrightarrow HXeO_4^-$$
$$2\,HXeO_4^- + 2\,OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 2\,H_2O$$

Perxenate solutions are yellow and are powerful oxidising agents.

Example 8.9
Give the formula of the noble gas species that is isostructural with (a) ICl_4^-, (b) IBr_2^-, (c) BrO_3^-

Solution
(a) XeF_4 (b) XeF_2 (c) XeO_3

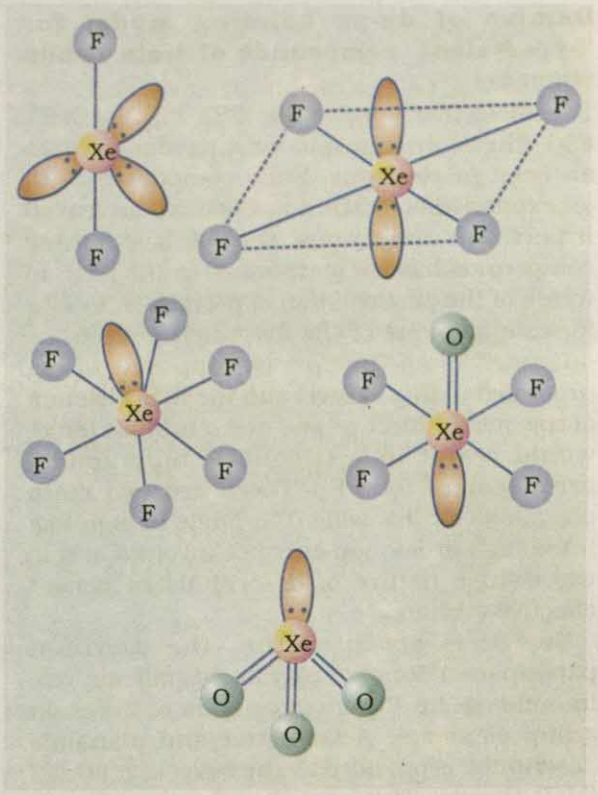


Fig. 8.16 *The structures of XeF_2, XeF_4, XeF_6, XeO_3 and $XeOF_4$.*

8.6.4 Uses of Noble Gases

Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs. It is also used in the laboratory for handling substances that are air-sensitive.

Helium is a non-flammable and light gas. Hence, it is used in filling balloons for meteorological observations. It is also used in gas-cooled nuclear reactors. Liquid helium (b.p. 4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures. It is used to produce and sustain powerful superconducting magnets which form essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis.

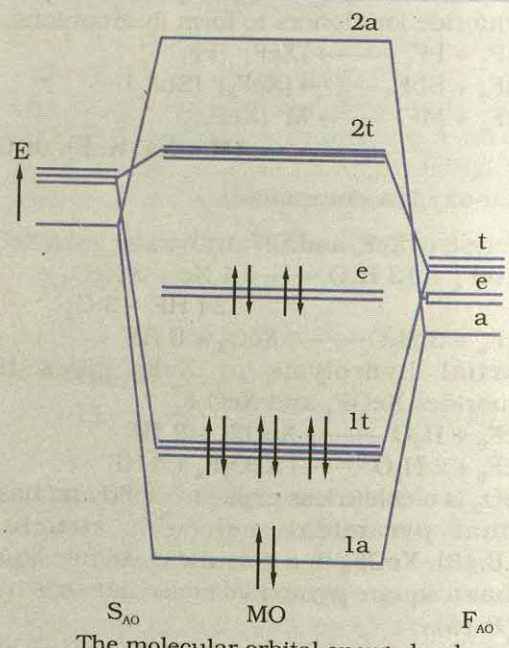
Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. There are no significant uses of xenon and krypton. They are used in light bulbs designed for special purposes.

Demise of dπ-pπ bonding model for 'hypervalent' compounds of Main Group elements

In molecular species like SF_6, PF_5, I^-_3, XeF_2 and others, the central atoms have more than an octet of electrons. Such compounds with an expanded octet (Unit 6, Class XI) are called hypervalent compounds. The bonding in these compounds has been explained in the past, in terms of the participation of *d*-orbitals. In PF_5, for example, one of the five valence electrons on the P atom ($3s^2 3p^3$) is supposed to get promoted to the *3d*-level and the hybridisation of the one *s*-, three *p*- and one *d* orbitals (sp^3d) would result in a trigonal - bipyramidal arrangement for PF_5. There are two main objections for involving *d*- orbitals in bonding: i) the high promotion energies involved and ii) the diffuse nature of *d* -orbitals to permit effective overlap.

Now it is accepted that the *d*-orbital participation does not play any significant role in bonding, involving compounds of the main group elements. A far better and plausible description is provided by the molecular orbital (MO) theory. This may be illustrated with reference to the SF_6 molecule. From the sulphur and fluorine atoms in the molecule, we have ten atomic orbitals from which ten molecular orbitals can be constructed by linear combination as shown in the diagram. The notations designating the AOs and MOs are symmetry notations which may be accepted as such. It can be seen that there are four bonding MOs and two non-bonding MOs followed by four anti-bonding MOs. Since we have to accommodate twelve electrons (6 from S and 6 from the six fluorines), the same will occupy the four bonding and the two non-bonding MOs in accordance with the Hund's rule. The formation of the SF_6 molecule is thus easily explained without invoking the participation of high energy *d*-orbitals.

A similar description can be used for the PF_5 molecule. Also multiple bonding in molecules or ions like SO_4^{2-} and ClO^-_4 which was previously explained in terms of the *dπ-pπ* interactions can now be explained in terms of the MO theory.



The molecular orbital energy level diagram of SF_6

SUMMARY

Groups 13 to 18 of the Periodic table of elements constitute the *p*-block. An overview of the Chemistry of these elements barring B, C, N and O is presented here.

In group 13, the characteristic group oxidation state of + 3 is known, but the + 1 state gets progressively stabilised on going down the group. It is particularly favoured by Tl. This is a consequence of the so called 'inert pair effect' which also accounts for the stability of the dipositive oxidation states of Sn and Pb and tripositive state of Bi. The hydrides and halides of Al to Tl are Lewis acids. The basic character of oxides of Al to Tl increases down the group.

Si, Ge, Sn and Pb form covalent compounds of the MX_4 type (X = H, Cl). On going down the group, the tendency to catenation decreases as C >> Si > Ge ≈ Sn > Pb. Si forms an

extensive range of silicate structures by linking of SiO_4 tetrahedra through Si – O – Si links. The Silicone polymers also contain Si – O – Si linkages with R_2SiO repeat units. Tin and lead form MO_2 and MO type oxides. Their chemistry is characterised by (+2) oxidation state. In general, the heavier *p*-block elements favour low oxidation states.

The most important element of group 15 is phosphorus. It exists in white, red and black allotropic forms. It forms molecular halides of PX_3 and PX_5 types and oxides P_4O_6 and P_4O_{10}. On descending the group the elements become increasingly basic. Thus, while oxides of P and As are acidic, antimony oxide is amphoteric and bismuth oxide is basic. Out of the several oxoacids of phosphorus, phosphoric acid is the most important.

The group 16 elements, S, Se, Te and Po form a variety of compounds in which they display predominantly covalent behaviour. Sulphur exists in several allotropic forms. Orthorhombic and monoclinic sulphur are more common. SO_2 and SO_3 are two important oxides of sulphur. They are used for the manufacture of sulphuric acid. Sulphuric acid has numerous applications. Polonium is a radioactive element.

F, Cl, Br, I and At (group 17) constitute the halogen family. These elements are extremely reactive and as such they are found in the combined state only. They form halide salts of the MX type or covalent compounds with E-X bonds (where X is a halogen). Fluorine is the most electronegative of all elements. It forms compounds with all other elements except He, Ne and Ar. Fluorine and chlorine are obtained by electrolysis of their halide salts. Bromine and iodine are obtained by the oxidation of bromides and iodides with chlorine. Halogens combine with one another to form interhalogen compounds of the type XX'_n (n = 1, 3, 5, 7). The acidity of hydrohalic acids decreases in the order HF < HCl < HBr < HI. The oxoacids of halogens are strong oxidising agents. Astatine is a rare radioactive element.

Noble gases (group 18), with closed valence shell electronic configuration exhibit low chemical reactivity. The real chemistry of these elements started in 1962 and the best characterised and studied compounds are the fluorides, oxides and acids of xenon. Krypton is known to form KrF_2 only.

EXERCISES

8.1 Name the principal ore of aluminium and describe how aluminium metal is extracted from this ore.

8.2 Explain why aluminium, though an electropositive metal, finds extensive use as a structural material.

8.3 Discuss the pattern of variation in the oxidation states of the following:
(i) Al to Tl (ii) Si to Pb and (iii) P to Bi

8.4 How is lithium aluminium hydride ($LiAlH_4$) prepared? What is its important use?

8.5 Write balanced equations for the following reactions:
(a) Aqueous sodium hydroxide is added dropwise to a solution of gallium chloride in water. A precipitate is formed initially which dissolves on further addition of NaOH solution.
(b) SnO is treated with dilute HNO_3
(c) Tin is heated with an excess of chlorine gas
(d) Lead sulphide is heated in air.

8.6 Name the principal ores of tin and lead and describe how these metals are extracted from their respective ores.

8.7 What is the importance of ultra pure elemental silicon? How is it obtained?

8.8 What are silicates? How are they classified?

8.9 What are silicones? How are they manufactured?

8.10 How far do you agree with the concept of 'inert pair effect'? Justify your answer.

8.11 State the difference in the properties and structures of white and red phosphorus.

8.12 Write balanced equations for the following reactions :

(a) $Ca_3P_2 + H_2O \longrightarrow$

(b) $P_4O_{10} + H_2O \longrightarrow$

(c) $As_4 + Cl_2$ (excess) $\longrightarrow$

(d) $P_4 + KOH + H_2O \longrightarrow$

8.13 Describe a method for the isolation of elemental phosphorus from $Ca_3(PO_4)_2$.

8.14 What is the oxidation state of phosphorus in the following: (a) H_3PO_3 (b) PCl_3 (c) Ca_3P_2 (d) Na_3PO_4 (e) POF_3

8.15 Calculate the volume of 0.1M NaOH solution required to neutralise the solution produced by dissolving 1.1 g of P_4O_6 in water.

8.16 Compare the structures of white phosphorus, P_4O_6 and P_4O_{10}.

8.17 Using VSEPR theory, predict the probable structures of SO_3^{2-} IF_6^- XeF_2 ClO_4^- ICl_4^- and IBr_2^-.

8.18 Starting from elemental sulphur, how would you prepare (a) H_2SO_4 (b) SCl_2 (c) SF_6

8.19 What are the oxidation states of S in the following compounds: (a) PbS (b) SO_2 (c) SF_6 (d) $Na_2S_2O_3$ (e) H_2SO_3.

8.20 Describe the contact process for the manufacture of sulphuric acid.

8.21 Write balanced equations for the following reactions:

(a) $Cu + \text{Conc. } H_2SO_4 \longrightarrow$

(b) $SF_4 + H_2O \longrightarrow$

(c) $H_2S + SO_2 \xrightarrow{\text{catalyst}}$

(d) $Te(s) + Cl_2(g) \longrightarrow$

8.22 How would you prepare:

(a) Cl_2 gas in the laboratory

(b) HF from CaF_2

(c) Br_2 from sea water

(d) I_2 from $NaIO_3$

(e) HBr from NaBr ?

8.23 Calculate the weight of HI obtained by the reaction of 62 g of red phosphorus with iodine in the presence of water.

8.24 Describe the chief uses of fluorine, chlorine and their compounds.

8.25 Write balanced equations for the following :

(a) NaCl is heated with sulphuric acid in the presence of MnO_2

(b) Chlorine gas is passed into a solution of NaI in water

(c) SiO_2 is treated with HF

(d) $NaClO_3$ is treated with SO_2

(e) Iodine is treated with conc. HNO_3.

8.26 How are xenon fluorides XeF_2, XeF_4 and XeF_6 prepared? Deduce their structures applying VSEPR theory.

8.27 How are XeO_3 and $XeOF_4$ prepared? Describe their molecular shapes.

8.28 How would you prepare the following:

(a) AsH_3 (b) H_3PO_3 (c) HI and (d) $HClO_4$?

8.29 Describe the molecular shapes of the following :

(a) SbF_3

(b) SF_4

(c) BrF_5

(d) IF_3.

8.30 Arrange the following in the order of property indicated for each set:

(a) F_2, Cl_2, Br_2, I_2 - increasing bond energy

(b) HF, HCl, HBr, HI - increasing acid strength

(c) M – F, M – Cl, M – Br, M – I - decreasing ionic character
(d) As_2O_3, ClO_2, GeO_2, Ga_2O_3 - increasing acidity
(e) NH_3, PH_3, AsH_3, SbH_3, BiH_3 – increasing base strength
(f) H_2O, H_2S, H_2Se, H_2Te – increasing acid strength
(g) HOCl, $HOClO$, $HOClO_2$, $HOClO_3$ – increasing acid strength.
(h) HOCl, HOBr, HOI – increasing acid strength

8.31 Find the oxidation state of the halogen in the following compounds:
(a) Cl_2O (b) ClO_2 (c) $KBrO_3$ (d) $NaClO_4$.

8.32 Define *catenation* and illustrate it with reference to sulphur chemistry.

8.33 Describe the shapes of the following species: (a) SiF_4 (b) SiF_6^{2-} (c) PF_5.

UNIT 9

THE *d*– AND *f*–BLOCK ELEMENTS

OBJECTIVES

After studying this Unit, you will be able to:

- justify the position of the *d*–and *f*–blocks of elements in the Periodic table.
- learn the electronic configurations of *d*–and *f*–block elements.
- know the general properties of the transition elements with special reference to group trends.
- know about the occurrence and extraction of iron, copper, zinc, and mercury.
- describe the preparation and properties of halides of silver and mercury, $K_2Cr_2O_7$, $KMnO_4$, $CuSO_4$ and $AgNO_3$, and learn about chemistry of photography.
- describe the properties of *f*-block elements (lanthanoids and actinoids).

"Iron, Copper, Silver and Gold - all are transition elements that have played important roles in the development of human civilization."

THE *d*–AND *f*–BLOCK ELEMENTS

The elements of *d*- and *f*- blocks of periodic table are commonly known as *transition* and *inner transition* elements respectively.

The three series: i) Sc to Zn, ii) Y to Cd and iii) La to Hg (excluding the elements Ce to Lu) mainly constitute the three transition series, while the lanthanoids and actinoids form the inner transition elements.

The presence of partly filled *d* or *f* orbitals in these elements sets the study of these elements and their compounds apart from that of the main group elements. However, the usual valence theory as applicable to the main group elements also holds for the transition elements.

The transition elements include precious metals such as silver, gold and platinum and industrially important metals like iron, copper and titanium.

In this Unit, we will first deal with the general properties of the *d*-block elements with special emphasis on the trends in properties of the first row (*3d*) elements, occurrence and extraction of some common transition metals, and the preparation and properties of some important compounds. This will be followed by consideration of certain important aspects of the chemistry of the inner transition elements (lanthanoids and actinoids).

THE TRANSITION ELEMENTS (*d*-block)

9.1 POSITION IN THE PERIODIC TABLE

The transition elements occupy the large middle section flanked by *s*- and *p*-blocks in the periodic table. In fact, the very name 'transition' is given to these elements because of their position between *s*- and *p*-block elements. The

penultimate shell of electrons in their atoms gets expanded from eight to eighteen by the addition of *d* electrons. The elements make up the three complete rows corresponding to the filling of 3*d*, 4*d*, and 5*d* orbitals. The fourth row which begins with the filling of 6*d* is still incomplete. These series of transition elements are shown in Table 9.1.

9.2 ELECTRONIC CONFIGURATIONS OF THE TRANSITION ELEMENTS

In general the electronic configuration of these elements is $(n-1)\ d^{1-10}\ n\ s^{1-2}$. The $(n-1)$ stands for the inner shell and the *d* orbitals may have one to ten electrons and the *s* orbital of the outermost shell (*n*) may have one or two electrons (Unit 3, Class XI). However, this generalization has several exceptions because there is very little difference in the energies of $(n-1)d$ and *ns* orbitals. Furthermore, half and completely filled subshells are relatively more stable. A consequence of this factor is reflected in the electronic configurations of Cr, Mn, Cu and Zn in the *3d* series of transition elements. The outer electronic configurations of the transition elements are given in Table 9.1.

Zinc, cadmium and mercury are the end members of the three respective series. Their electronic configuration is represented by the general formula $(n-1)d^{10}n\,s^2$. The *d* orbitals in these elements are completely filled in the ground state and in their common oxidation states. Therefore, these are often not regarded as transition elements.

Transition elements with partly filled *d*-orbitals exhibit certain characteristic properties. For example, they display a variety of oxidation states, form coloured ions and enter into complex formation with different anions and neutral molecules. These metals and their compounds also exhibit catalytic property and many of them show paramagnetic behaviour. There are greater horizontal similarities in the properties of the transition elements in contrast to the main group elements. However, some group similarities also exist. We shall first study the general properties and their trends in the horizontal rows and then consider some group similarities.

Example 9.1
On what ground can you say that scandium ($Z = 21$) is a transition element but zinc ($Z = 30$) is not?

Table 9.1 Outer electron configurations of the transition elements (ground state)

					1st Series					
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10
					2nd Series					
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10
					3rd Series					
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10
					4th Series					
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub
Z	89	104	105	106	107	108	109	110	111	112

Solution

On the basis of incompletely filled *3d* orbitals in case of scandium ($3d^1$), and completely filled in case of Zn ($3d^{10}$), they are considered transition and non-transition elements respectively.

9.3 PROPERTIES OF TRANSITION ELEMENTS

9.3.1 Physical Properties

Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity, and metallic lustre. Except mercury which is a liquid at room temperature, other transition elements have typical metallic structures.

Their melting and boiling points are high. Fig. 9.1 depicts the melting points of the *3d*, *4d*, and *5d* transition metals. The high melting points are attributed to strong interatomic bonding, which involves the participation of both *ns* and (*n*-*1*) *d* electrons. In any row, the melting points of these metals rise to a maximum at d^6 except for anomalous values of Mn and Tc and fall regularly as the atomic number increases.

With the exception of zinc, cadmium and mercury, the transition elements are much harder and less volatile. They exhibit high enthalpies of atomization (Fig. 9.2); the maxima at about the middle of each series indicate that one unpaired electron per *d* orbital is particularly favourable for strong interatomic interaction. In general, greater the number of valence electrons, stronger is the resultant bonding. Since the enthalpy of atomization is an important factor in determining the standard electrode potential of a metal, those with highest enthalpy of atomization tend to be noble metals.

Another interesting generalization that may be drawn from Fig. 9.2 is that the metals of the second (*4d*) and third (*5d*) series have greater enthalpies of atomization than the corresponding elements of the first series; this is an important factor for their having much more frequent metal-metal bonding in their compounds.

The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements. Thus, from titanium to copper the increase in density may be noted (Table 9.2).

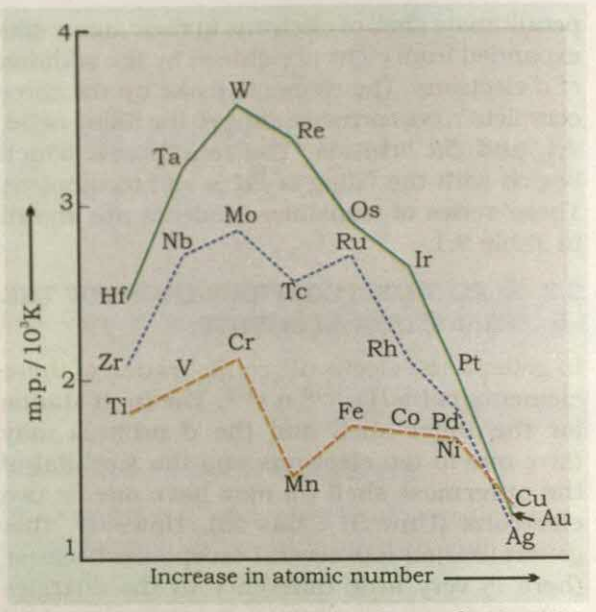


Fig. 9.1 *Trends in melting points of transition elements.*

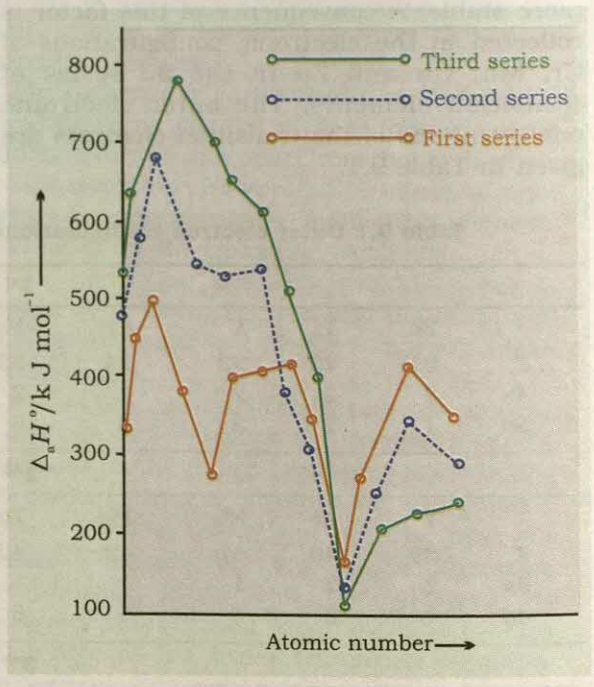


Fig. 9.2 *Trends in enthalpies of atomization of transition elements.*

9.3.2 Variations in Atomic and Ionic Sizes

In general, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. This is because the extra electron enters a *d* orbital each time the

Table 9.2 Electronic configurations and some other properties of the first series of transition elements

Element		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number		21	22	23	24	25	26	27	28	29	30
Electronic configuration											
	M	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
	M^+	$3d^1 4s^1$	$3d^2 4s^1$	$3d^3 4s^1$	$3d^5$	$3d^5 4s^1$	$3d^6 4s^1$	$3d^7 4s^1$	$3d^8 4s^1$	$3d^{10}$	$3d^{10} 4s^1$
	M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
	M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$
Enthalpy of atomization/kJ mol^{-1}		326	473	575	397	281	416	425	430	339	126
Ionization enthalpy/ kJ mol^{-1}											
	I	631	656	650	653	717	762	758	736	745	906
	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
	III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829
r/pm	M	164	147	135	129	137	126	125	125	128	137
	M^{2+}	-	-	79	82	82	77	74	70	73	75
	M^{3+}	73	67	64	62	65	65	61	60	-	-
$E^\ominus$/V											
	M^{2+}/M	-	-	-1.18	-0.90	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76
	M^{3+}/M^{2+}	-	-	-0.26	-0.41	+1.57	+0.77	+1.97	-	-	-
Density/g cm^{-3}		3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

nuclear charge increases by unity. The shielding effect of a *d* electron is small, the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases. The atomic radius also decreases in the same way. The variation within a series is quite small. An interesting point emerges when sizes of elements in one series are compared with the sizes of the corresponding elements in other series. The data in Fig. 9.3 shows an increase from the first (3*d*) to the second (4*d*) series of the elements but the radii of the third (5*d*) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the 4*f* orbitals, which must be filled before the 5*d* series of elements begin. The filling of 4*f* before 5*d* orbital results in a regular decrease in atomic radii called **lanthanoid contraction** which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the corresponding elements of second and the third *d* series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties.

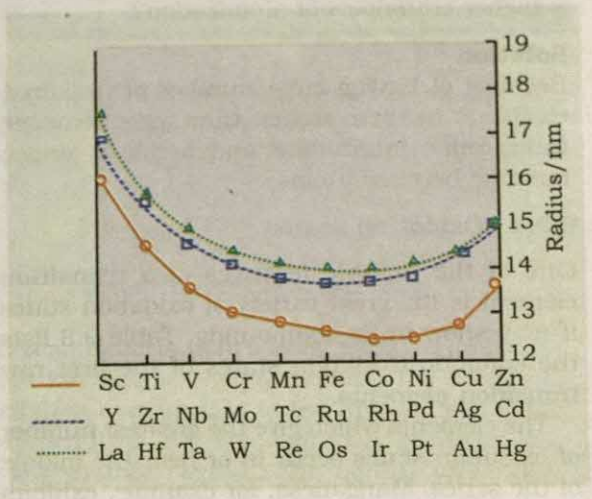


Fig. 9.3 *Trends in atomic radii of transition elements.*

9.3.3 Ionization Enthalpies

With increasing nuclear charge, which accompanies the filling of the inner *d* orbitals, there is an increase in ionization enthalpy along each series of the transition elements from left to right, but many small variations occur. Table 9.2 gives the values for the first three ionization enthalpies of the first row elements. These values show that although the first ionization enthalpy, in general, increases, the increase in the second and third ionization enthalpies for the successive elements are not of the same magnitude. However, the trend is similar for the second ionization enthalpies, which for the most part increase smoothly as the atomic number increases, the exceptions are chromium and copper for which these values are notably larger than those of their neighbours. These exceptions are attributed to the extra stability of half-filled or completely filled set of *d* orbitals in chromium and copper. The third ionization enthalpies are quite high and there is a marked break between the values for Mn^{2+} and Fe^{2+}. Also, the high values for copper, nickel and zinc indicate why it is difficult to obtain oxidation state greater than two for these elements.

Although ionization enthalpies give some guidance concerning the relative stabilities of oxidation states, this problem is very complex one and not amenable to ready generalization.

Example 9.2
Why do the transition elements exhibit higher enthalpies of atomization?

Solution
Because of having large number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between atoms.

9.3.4 Oxidation States

One of the notable features of a transition element is the great variety of oxidation states it may show in its compounds. Table 9.3 lists the common oxidation states of the first row transition elements.

The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. The lesser number of oxidation states at the extreme ends

Table 9.3 Oxidation states of the first row transition metals (the most common ones are in coloured bold types)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+1	
								+2	+2
+3	+3	+3	+3	+3	+3	+3	+3		
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

stems from either too few electrons to lose or share (Sc, Ti) or too many *d* electrons (hence fewer orbitals available in which to share electrons with others) for higher valence (Cu, Zn). Thus, early in the series scandium(II) is virtually unknown and titanium(IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (no *d* electrons are involved). The maximum oxidation states of reasonable stability correspond in value to the sum of the *s* and *d* electrons upto manganese ($Ti^{IV}O_2$, $V^{V}O_2^{+}$, $Cr^{VI}O_4^{2-}$, $Mn^{VII}O_4^{-}$) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are $Fe^{II,III}$, $Co^{II,III}$, Ni^{II}, $Cu^{I,II}$, Zn^{II}.

The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of *d* orbitals in such a way that their oxidation states differ from each other by unity, e.g., V^{II}, V^{III}, V^{IV}, V^{V}. This should be contrasted with the variability of oxidation states of non-transition elements where oxidation states normally differ by units of two.

9.3.5 Chemical Reactivity and $E^{\ominus}$ Values

Transition metals vary widely in their chemical reactivity. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble'—that is, they are unaffected by simple acids.

The metals of the first series with the exception of copper are relatively more reactive and are oxidised by 1M H^+, though the actual rate at which these metals react with oxidizing agents like hydrogen ion (H^+) is sometimes slow. For example, titanium and vanadium, in practice, are passive to dilute non-oxidising acids at room temperature. The $E^{\ominus}$ values for

M^{2+}/M (Table 9.2) indicate a decreasing tendency to form divalent cations across the series. This general trend towards less negative $E^{\ominus}$ values is related to the general increase in the sum of the first and second ionization enthalpies. It is interesting to note that the values $E^{\ominus}$ for Mn, Ni, and Zn are more negative than expected from the general trend. Whereas the stabilities of half-filled *d* subshell (d^5) in Mn^{2+} and completely filled *d* subshell (d^{10}) in zinc are related to their $E^{\ominus}$ values; for nickel, $E^{\ominus}$ value is related to the highest negative enthalpy of hydration.

An examination of the $E^{\ominus}$ values for the redox couple M^{3+}/M^{2+} (Table 9.2) shows that Mn^{3+} and Co^{3+} ions are the strongest oxidising agents in aqueous solutions. The ions Ti^{2+}, V^{2+} and Cr^{2+} are strong reducing agents and will liberate hydrogen from a dilute acid, e.g.

$$2\ Cr^{2+}(aq) + 2\ H^{+}(aq) \rightarrow 2\ Cr^{3+}(aq) + H_2(g)$$

9.3.6 Magnetic Properties

When a magnetic field is applied to substances, two types of magnetic behaviour are observed: *diamagnetism* and *paramagnetism* (Unit 2). Diamagnetic substances are repelled by the applied field while the paramagnetic substances are attracted. Substances which are attracted very strongly are said to be *ferromagnetic*. In fact, ferromagnetism is an extreme form of *paramagnetism*. Many of the transition metal ions are paramagnetic, i.e., attracted by a magnetic field.

Paramagnetism arises from the presence of unpaired electrons. Each such electron has a magnetic moment associated with its *spin angular momentum* and *orbital angular momentum*. For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula, i.e.,

$$\mu = \sqrt{n(n+2)}$$

Where n is the number of unpaired electrons and μ is the magnetic moment in Bohr magneton(μ_B) units[1]. A single 1*s* electron has a magnetic moment of 1.73 Bohr magnetons (μ_B).

The magnetic moment increases with the increasing number of unpaired electrons. Thus, the observed magnetic moment gives a useful indication about the number of unpaired electrons present in the atom, molecule or ion. The magnetic moments calculated from the 'spin-only' formula and those derived experimentally for some ions of the first row transition elements are given in Table 9.4. The experimental data are mainly for hydrated ions in solution or in the solid state.

Table 9.4 Calculated and observed magnetic moments (μ_B)

Ion	Configuration	Unpaired electron	Magnetic moment calculated	Magnetic moment observed
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Ti^{2+}	$3d^2$	2	2.84	2.76
V^{2+}	$3d^3$	3	3.87	3.86
Cr^{2+}	$3d^4$	4	4.90	4.80
Mn^{2+}	$3d^5$	5	5.92	5.96
Fe^{2+}	$3d^6$	4	4.90	5.3-5.5
Co^{2+}	$3d^7$	3	3.87	4.4-5.2
Ni^{2+}	$3d^8$	2	2.84	2.9-3.4
Cu^{2+}	$3d^9$	1	1.73	1.8-2.2
Zn^{2+}	$3d^{10}$	0	0	

Example 9.3
Evaluate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

Solution
With atomic number 25, the divalent ion in aqueous solution will have d^5 configuration (five unpaired electrons). The magnetic moment, μ is

$$\mu = \sqrt{5(5+2)} = 5.92\,\mu_B$$

9.3.7 Formation of Coloured Ions

When an electron from a lower energy *d* orbital is excited to a higher energy *d* orbital, the energy of excitation corresponds to the frequency of light absorbed (Unit 10). This frequency generally lies in the visible region. The colour observed

[1] ($\mu_B = eh/4\ m = 9.27 \times 10^{-24}$ A m^2 or J T^{-1})

corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand. In aqueous solutions where water molecules are the ligands, the colour of the ions observed are listed in Table 9.5. A few coloured solution of *d*-block elements are illustrated below the table.

Table 9.5 The colours of Some of the First Row Transition Metal Ions (aquated)

Configuration	Example	Colour
$3d^0$	Sc^{3+}	colourless
$3d^0$	Ti^{4+}	colourless
$3d^1$	Ti^{3+}	purple
$3d^1$	V^{4+}	blue
$3d^2$	V^{3+}	green
$3d^3$	V^{2+}	violet
$3d^3$	Cr^{3+}	violet
$3d^4$	Mn^{3+}	voilet
$3d^4$	Cr^{2+}	blue
$3d^5$	Mn^{2+}	pink
$3d^5$	Fe^{3+}	yellow
$3d^6$	Fe^{2+}	green
$3d^7$	Co^{2+}	pink
$3d^8$	Ni^{2+}	green
$3d^9$	Cu^{2+}	blue
$3d^{10}$	Zn^{2+}	colourless

Colours of some of the first row transition metal ions in aqueous solutions. From left to right; V^{4+}, V^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} .

9.3.8 Formation of Complex Compounds

Complex compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species with characteristic properties. A few examples are : $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$. (The chemistry of complex compounds is dealt with in detail in Unit 10). The transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of *d* orbitals for bond formation.

9.3.9 Catalytic Properties

The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (Contact Process), finely divided iron (Haber's Process), and nickel (Catalytic Hydrogenation) are some of the examples. Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise *3d* and *4s* electrons for bonding); this has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowered). Also because the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulphate ions,

$$2\ I^- + S_2O_8^{2-} \rightarrow I_2 + 2\ SO_4^{2-}$$

An explanation of this catalytic action can be given as:

$$2\ Fe^{3+} + 2\ I^- \rightarrow 2\ Fe^{2+} + I_2$$

$$2\ Fe^{2+} + S_2O_8^{2-} \rightarrow 2\ Fe^{3+} + 2\ SO_4^{2-}$$

9.3.10 Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, N or C are trapped inside the crystal lattices of metals. They are usually non-stoichiometric and are neither typically ionic nor covalent. Many of the transition metals form interstitial compounds particularly with small non-metal atoms such as hydrogen, boron, carbon and nitrogen. These small atoms enter into the voids sites between the packed atoms of the crystalline metal, e.g., TiC, Mn_4N, Fe_3H, TiH_2, etc. The formulae quoted do not, of course, correspond to any normal oxidation state of the metal and often non-stoichiometric material is obtained with such composition as $VH_{0.56}$ and $TiH_{1.7}$. Because of the nature of their composition, these compounds are referred to as *interstitial compounds*. The principal physical and chemical characteristics of these compounds are as follows:

(i) They have high melting points, higher than those of pure metals.
(ii) They are very hard, some borides approach diamond in hardness.
(iii) They retain metallic conductivity.
(iv) They are chemically inert.

9.3.11 Alloy Formation

An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys; chromium, vanadium, tungsten, molybdenum, and manganese are used for the production of variety of steels and stainless steel. Alloys of transition metals with non-transition metals such as brass (copper-zinc), and bronze (copper-tin) are also of considerable industrial importance.

Example 9.4

For the first row transition metals the $E^{\ominus}$ values are

$E^{\ominus}$	V	Cr	Mn	Fe	Co	Ni	Cu
(M^{2+}/M)	−1.18	−0.91	−1.18	−0.44	−0.28	−0.25	+0.34

Explain the irregularity in the above values.

Solution

The $E^{\ominus}(M^{2+}/M)$ values are not regular which can be explained from the irregular variation of ionization energies ($I E_1 + II E_2$) and also the sublimation energies which are relatively much less for manganese and vanadium. (240 kJ mol^{-1} for manganese and 470 kJ mol^{-1} for vanadium).

Example 9.5

Explain as to why the $E^{\ominus}$ value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}.

Solution

Much larger third ionization energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.

9.4 COMPARISON OF THE FIRST ROW TRANSITION METALS THROUGH THE *d* ELECTRON CONFIGURATION

The d^0 configuration: Of the simple ions, only Sc^{3+} is known to have this configuration. This configuration then occurs for those metals in which the formal oxidation states equal the total number of *3d* and *4s* electron. This is true for Ti(IV), V(V), Cr(VI), and Mn(VII) but for Fe (VIII) is unknown.

The d^1 configuration: Except vanadium(IV), all others with this configuration are either reducing or undergo disproportionation. For example, disproportionation occurs for Cr(V) and Mn (VI) as follows:

$$3\ CrO_4^{3-} + 8\ H^+ \rightarrow 2\ CrO_4^{2-} + Cr^{3+} + 4\ H_2O$$

$$3\ MnO_4^{2-} + 4\ H^+ \rightarrow 2\ MnO_4^- + MnO_2 + 2\ H_2O$$

The d^2 configuration: This configuration ranges from Ti^{II} which is very strongly reducing, to Fe^{VI}, which is very strongly oxidising. Vanadium (III) is also reducing.

The d^3 configuration: Chromium (III) is the important species with this configuration which is stable and well known for complex formation. In other cases, this configuration is relatively unimportant.

The d^4 configuration: There are really no stable species with this configuration. The chromium(II) is strongly reducing and manganese(III) disproportionates.

The d^5 configuration: The two important species with this configuration are Mn^{2+} and Fe^{3+}, the latter may, however, be reduced to Fe^{2+}.

The d^6 configuration: Iron(II) and cobalt(III) are important species with this configuration. Iron(II) is quite stable although a mild reducing agent and cobalt(III) is stable in the presence of strong complexing reagents.

The d^7 configuration: The species with this configuration is cobalt(II) which is stable in aqueous solutions but gets oxidised to form Co(III) complexes in the presence of strong ligands.

The d^8 configuration: Nickel(II) is the most important species with this configuration.

The d^9 configuration: This configuration is found in Cu^{2+} compounds and is by far the most important in the chemistry of copper. Otherwise, this configuration is of little importance.

The d^{10} configuration: The two species Cu^+ and Zn^{2+} are important with this configuration. Whereas, copper(I) is easily oxidised to copper(II), zinc(II) is the most stable state known for zinc.

9.5 GENERAL GROUP[2] TRENDS IN THE CHEMISTRY OF THE *d*-BLOCK METALS

Group 4 consists of elements–titanium (22), zirconium (40) and hafnium (72). They are

[2] *Group three consists of elements - scandium (21), yttrium(39) and lanthnum (57) whose study is considered along with lanthnoids.*

lustrous silvery metals with high melting points. These elements are relatively electropositive but less so than those of Group 3. If heated, they react directly with most non-metals, particularly with oxygen, hydrogen (reversibly) and in case of titanium, with nitrogen also. With the exception of hydrofluoric acid, mineral acids have little effect unless hot. The most stable oxidation state is +4. The lower oxidation states are not known for zirconium and hafnium. Even for titanium, they are easily oxidised to +4 state. Some typical compounds are chlorides, $TiCl_4$, $ZrCl_4$ and $HfCl_4$, and oxides TiO_2, ZrO_2 and HfO_2. Zirconium and hafnium, because of the similarity of their atomic radii (Zr 160pm, Hf 159pm), exhibit similar properties.

Group 5 consists of elements–vanadium, niobium and tantalum. In many ways these elements are similar to the elements of Group 4. They are shiny silvery metals and keeping with the trend, slightly less positive than their predecessors. As a consequence of the lanthanoid contraction, the heavier pair niobium and tantalum is virtually identical in size and exhibits similar properties. Although each of these elements shows all the formal oxidation states from +5 down to +1, the most stable one in case of vanadium is +4. By contrast, the chemistry of niobium and tantalum is confined to the group oxidation state of +5. Vanadium exhibits all the oxidation states, +5, +4, +3 and +2 in its compounds. The chief use of vanadium is to increase the strength and toughness of steel.

Group 6 consists of the elements–chromium, molybdenum and tungsten which are silvery, lustrous and fairly soft (when pure). The group oxidation state of +6 is exhibited by all the three elements in their oxoanions. For chromium, +3 is the most stable state in aqueous solution and in complexes. Chromium(II) is strongly reducing. The chemistry of molybdenum and tungsten in lower oxidation states is rather complicated because of the presence of strong M-M multiple bonding. Chromium is used in leather industry and in the manufacture of stainless steel and chrome plating, molybdenum is used in X-ray tubes and compounds of molybdenum and tungsten are employed as catalysts.

Group 7 elements are manganese, technetium and rhenium. Technetium is radioactive and is mainly obtained from fission waste. Rhenium is rare and closely resembles technetium in its properties. Manganese exhibits all the oxidation states from +2 to +7 of which the important ones are +2, +4 and +7. Manganese is an important constituent of all steels. Rhenium is used in electronic filaments, high temperature thermocouples and in flash bulbs.

Group 8 consists of iron, ruthenium and osmium. Ruthenium and osmium are stable to atmospheric attack. By contrast, iron is subject to corrosion in the rusting. Whereas iron fails to attain the group oxidation state (+8), ruthenium and osmium attain the oxidation state of +8, though they are the only elements to do so in their respective series. The lower oxidation states of +2 and +3, which are so well known for iron are practically unknown for ruthenium and osmium. Iron is the most important metal of commerce and industry in the form of steel in the world.

Group 9 elements are cobalt, rhodium and iridium. Cobalt is appreciably less reactive than iron. The most common oxidation states of cobalt are +2 and +3, but the latter in aqueous solution, is a strong oxidising agent; it can oxidise even water with the evolution of oxygen. For rhodium and iridium, +3 state is the most important, though the oxidation state of +4 is occasionally found with iridium. Co^{III} exhibits unique tendency of forming a large number of coordination complexes especially with N-donor ligands. Cobalt compounds find use in ceramic and paint industries and as catalysts.

Group 10 consists of elements–nickel, palladium and platinum. In the bulk state none of these is reactive and indeed are resistant to atmospheric corrosion at normal temperatures. Nickel and palladium react on heating with certain non-metals such as halogens. However, the reactivity falls from nickel through palladium to platinum. The oxidation state of +2 is important for nickel and palladium; for platinum both the +2 and +4 oxidation states are equally important. Nickel is well known as an alloying metal, e.g., *nichrome* (60% Ni, 40% Cr) and *german silver* (Cu 25-30%, Zn 25-30% and Ni 40-50%). Most extensive uses of palladium and platinum are as catalysts.

Group 11 consists of copper, silver and gold in the respective series. The reactivity decreases down the group and in its inertness gold resembles platinum metals. The best known oxidation states in aqueous solution are +2 for

copper, +1 for silver and +3 for gold. This agrees with their ionization energies; silver has the lowest first ionisation energy, the sum of the first and second is lowest for copper and the sum of the first, second and the third is the lowest for gold. The elements are, however, not well-related in their chemical behaviour. 'Horizontal' similarities with their neighbours in the periodic table are in fact more noticeable than vertical ones.

Group 12 consist of zinc, cadmium and mercury. Chemically, zinc and cadmium are rather similar and mercury is somewhat distinct. The compounds of these elements are characterised by the d^{10} configuration in which with the exception of Hg_2^{2+} ion, which formally involves Hg^{I}, they almost exclusively involve M^{II}. In view of the filled d subshell, these elements show few of the characteristic properties of transition elements and hence are not regarded as such.

Example 9.6
What is meant by 'disproportionation' of an oxidation state? Give an example.

Solution
When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation. For example, manganese(VI) becomes unstable relative to manganese(VII) and manganese(IV) in acidic solution.

$$3\ Mn^{VI}O_4^{2-} + 4\ H^+ = 2\ Mn^{VII}O_4^- + Mn^{IV}O_2 + 2H_2O$$

9.6 OCCURRENCE AND PRINCIPLES OF EXTRACTION OF SOME d-BLOCK METALS

You studied the general principles of extraction of elements in your Class XI, Unit 10. Here we deal with the occurrence and principles of extraction of a few d-block metals individually.

9.6.1 Iron

Occurrence

Iron is the second most abundant metal after aluminium in the earth's crust. The most important ores are *haematite* (Fe_2O_3), *magnetite* (Fe_3O_4) and *siderite* ($FeCO_3$). *Iron pyrites* (FeS_2), is also common, but owing to its higher sulphur content, it is not used for the production of iron. The earth's core is believed to consist mainly of iron (Class XI, Unit 4). Iron ore reserves in India are estimated at 75 million tonnes.

Extraction

The ore is usually first calcined to remove most of the water, to decompose carbonates and to oxidise sulphides. A charge of the calcined ore, limestone and coke is fed into the top of the blast furnace (Fig. 9.4). A blast of air preheated at about 1000 K is blown in by means of narrow pipes (tuyeres) at the base of the furnace. The burning of coke to carbon monoxide supplies most of the heat needed for the working temperature of the furnace which ranges from 1800 K at the bottom to about 500 K at the top. In the top part of the furnace, the reducing agent is carbon monoxide but at the bottom it is carbon itself. The typical reactions in the upper part are:

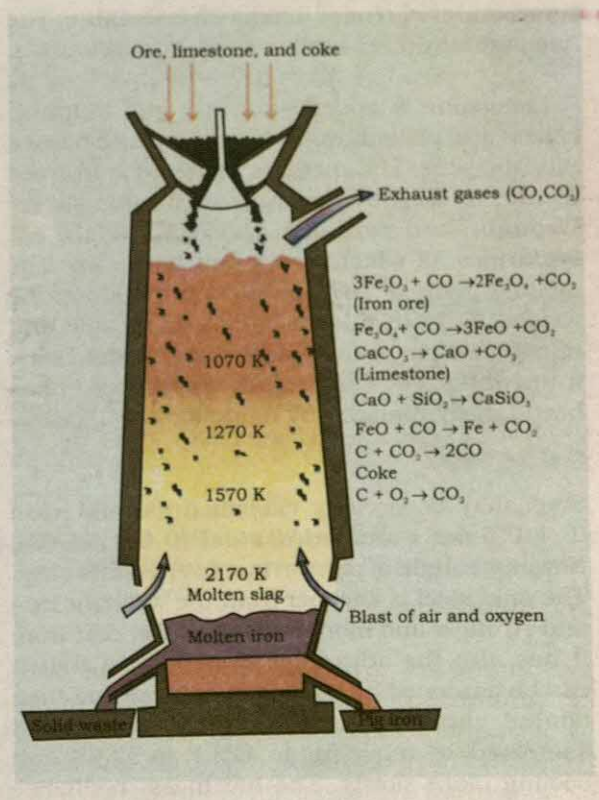


Fig 9.4 *Blast Furnace.*

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$
$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$$
$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$

In the lower hotter part, the main reaction is

$$FeO + C \rightarrow Fe + CO$$

The molten iron formed in the lowest zone runs down to the base. The limestone decomposes at about 1000 K to produce calcium oxide which combines with silica to form a *slag* of molten calcium silicate. The product known as *pig iron* contains about 4% of carbon and many other impurities (such as S, P, Si and Mn). Pig iron can be cast into variety of shapes in moulds. *Cast iron* is specially made by igniting pig iron with scrap iron and coke in specially designed furnaces by a blast of hot air. Cast iron contains about 3% carbon. It expands slightly on solidifying and, therefore, reproduces the shape of the mould. It is extremely hard but brittle. The melting point of cast iron is about the same as that of pig iron (~1473 K).

Wrought Iron or Malleable Iron

The purest form of commercial iron is made by oxidizing the impurities in cast iron in a reverberatory furnace lined with haematite. The haematite oxidizes carbon to carbon monoxide.

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

Limestone is added as a flux and sulphur, silicon and phosphorus are oxidized and passed into the slag. The metal is removed and freed from the slag by passing through rollers. Wrought iron contains approximately 0.5% impurities, of which about half is carbon. The melting point is 1673 K but the metal can be welded at 1273 K. It is tough, malleable and ductile and can be used for making chains, bolts, frameworks, etc. For structural purposes, it has been largely replaced by mild steel.

9.6.2 Steel

Steel may be broadly classified as *mild steel* (0.1-0.5% C) and *hard steel* (0.6-1.5% C). Nowadays, bulk of pig iron is converted into steel. The mild steel is cheaper than the wrought iron and stronger and more workable than cast iron; it has also the advantage over both in that it can be hardened by heating to redness and then cooled rapidly (quenching) in water and 'tempered' by reheating to 473 K to 573 K and cooling more slowly. The hardness, resilience and ductility can be controlled by varying the temperature and the rate of cooling as well as the precise composition of the steel.

Alloy steels with their enormous variety of physical properties are prepared by the addition of the appropriate alloying metal or metals (e.g., Mn, Cr, Ni, W). Thus, stainless steel contains about 18 percent of chromium; tungsten steel (which is very hard) about 5 percent of tungsten; and manganese steel (which is very tough) about 13 percent of manganese. The role of carbon in steel is a specialised topic which we shall not discuss here.

Steel making is undergoing rapid revolution and the old Bessemer and Open-Hearth processes are becoming obsolete. Among the modern methods are Basic Oxygen Process, Electric Arc Process and High-Frequency Induction Process. These processes utilize scrap steel and alloy scrap for making highly alloyed steels (see Box).

Steel Making Processes

(1) Bessemer Process

The molten pig iron is fed into a converter at a temperature of about 1473 K. A blast of oxygen diluted with either steam or carbon dioxide is blown through the converter. Oxygen reacts with impurities and raises the temperature to 2173 K. Carbon is oxidised to carbon monoxide which burns off at the mouth of the converter; oxides of silicon and manganese form slag. After about ten minutes, the flame dies down indicating that all carbon has been removed. The flame is stopped, slag is tapped off and then other metals (Mn, Cr, Ni and W) may be added towards the end of the operation to produce the required type of steel.

(2) Open-Hearth Process

In this process, a mixture of molten pig iron, scrap steel and limestone is heated on a shallow hearth furnace by producer gas. The furnace is adapted for different types of pig iron feed by using acidic or basic lining. The impurities are oxidised by the iron oxide present which form slag by combining with the lining. Thus,

$$3\,C + Fe_2O_3 \rightarrow 2\,Fe + 3\,CO$$

Oxides of P and Si + lining (CaO + MgO)
→ phosphate and silicate slag

Towards the end (after about ten hours) an alloy of Mn, Fe, and C (*spiegeleisen*) is added together with alloying metals.

The Open-Hearth process has advantages over the Bessemer's process largely because of the greater ease with which the composition of the steel can be controlled and greater fuel economy.

(3) The Oxygen Top-Blowing Process

In this process, liquid iron from the blast furnace is charged into a converter, scrap steel is added and a jet of oxygen is blown through a retractable steel 'lance' into or over the surface of the liquid metal. Impurities are oxidized and with the addition of lime form slag, which is usually removed by tilting the converter. When steel of desired composition is obtained, the oxygen is turned off and the molten steel is poured into laddler for casting into ingots.

(4) The Electric Arc Process

A charge of scrap steel and turnings is fed into the furnace and is melted by electric arc struck between adjustable carbon electrodes. Again, acidic or basic linings are employed for scrap differing in phosphorus content. This method is widely used in the manufacture of alloys and other high quality steels such as stainless steel and high-speed cutting steel.

(5) The High-Frequency Induction Process

A charge of alloy scrap of known composition, together with iron is fed into the furnace. Alternating current at 500-2000 Hz per second passes through the insulated water-cooled copper coils. The resulting magnetic field sets up steady current, which generates heat. The circulation of the metal caused by these currents produces strong stirring effect. The induction furnace is capable of producing high quality alloy steels containing tungsten, vanadium, chromium, manganese, molybdenum, cobalt and nickel for making ball-bearing, magnets, dies and tool steel etc.

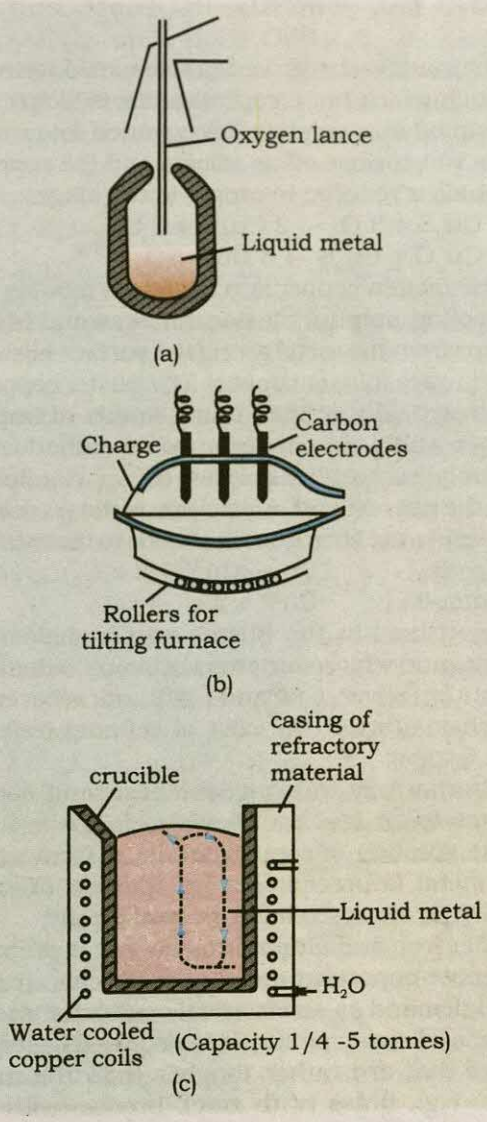


Fig. 9.5 *(a) The oxygen top-blowing process. (b) Electric arc process (c) High-frequency induction process.*

9.6.3 Copper

Occurrence

Copper does not occur abundantly in nature (about 1×10^{-4} % of the earth's crust). The chief ore of copper is *copper pyrites*, $CuFeS_2$. The ores of much less importance include *malachite*, $CuCO_3.Cu(OH)_2$, *cuprite*, Cu_2O and the *copper glance*, Cu_2S.

Extraction

Though native copper (in extremely pure form) is found near lake superior in America, copper is mainly extracted from copper pyrites. The sulphide ore is usually very low grade and is associated with iron sulphide, gangue and smaller quantities of arsenic, antimony, selenium, tellurium, silver, gold and platinum. The sulphide ore is first concentrated by froth-floatation process and then roasted in a current of air in a reverberatory furnace below the fusion point when arsenic and sulphur are driven off as volatile oxides. The temperature is then allowed to rise above the fusion point and limestone or silica is added. Iron(II) oxide slags off as iron silicate and the copper *matte* consisting of a mixture of copper(I) sulphide and iron(II) sulphide remains.

$$FeO + SiO_2 \rightarrow \underset{\text{slag}}{FeSiO_3}$$

The matte is charged into a silica-lined converter through which hot compressed air is blown. The remaining iron sulphide is converted into iron(II) oxide which slags off as silicate and the copper(I) sulphide is reduced to copper in two stages:

$$2\ Cu_2S + 3\ O_2 \rightarrow 2\ Cu_2O + 2\ SO_2$$
$$2\ Cu_2O + Cu_2S \rightarrow 6\ Cu + SO_2$$

The molten copper is run off into moulds and on cooling, sulphur dioxide, nitrogen and oxygen escape from the metal giving the surface blistered appearance (blister copper). The blister copper is electrolytically refined using anode of impure copper and pure copper strip as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode.

Anode: $Cu \rightarrow Cu^{2+} + 2\ e^-$

Cathode: $Cu^{2+} + 2\ e^- \rightarrow Cu$

Impurities in the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum, recovery of which may meet the cost of refining (refer to Unit 5 also).

Alternatively, prolonged exposure of copper pyrites to air and rain leads to formation of a dilute solution of copper sulphate, from which the metal is precipitated by addition of scrap iron. It is always refined electrolytically.

After iron and aluminium, copper is probably the most important metal of commerce. It is in great demand as an electrical conductor and for water and steam piping. It is also used in several alloys that are rather tougher than the metal itself, e.g., brass (with zinc), bronze (with tin) and coinage alloy (with nickel).

9.6.4 Silver

Occurrence

Silver occurs native often alloyed with copper, gold and platinum metals. An important ore of silver is the sulphide, *argentite* or *silver glance*, Ag_2S. Ores of lesser importance are *pyrargyrite* or *ruby silver* (Ag_3SbS_3), *proustite* (Ag_3AsS_3), and *horn silver* (AgCl). Silver is also worked up from the residues remaining after the isolation of copper, lead and gold.

Extraction

The most important method of extraction of silver is the cyanide process. The method involves leaching of the crude metal or ore with sodium cyanide solution (0.5 % or less concentration) through which air is blown. Silver goes into solution as complex cyanide and the pure metal is precipitated by the addition of zinc.

$$4\ Ag + 8\ CN^- + O_2 + 2\ H_2O \rightarrow 4\ [Ag(CN)_2]^- + 4OH^-$$
$$2\ Ag_2S + 8\ CN^- + O_2 + 2\ H_2O \rightarrow 4\ [Ag(CN)_2]^- + 2S + 4OH^-$$
$$2\ [Ag(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2\ Ag$$

The precipitate of silver is collected, dried and melted with a flux (borax or KNO_3) to oxidize lead and zinc impurities. Silver thus obtained is refined electrolytically.

Silver is also removed by desilverisation of lead obtained from argentiferrous lead through the concentration and smelting process. About one third of silver produced in the world is used in photography. It is also used in silverware and jewellery for silvering mirrors and in high capacity batteries.

9.6.5 Zinc

Occurrence

The chief ore of zinc is the sulphide, *zinc blende*, ZnS. It is also found as carbonate, *calamine*, $ZnCO_3$ and the oxide, *zincite*, ZnO. A few silicate minerals, e.g., *willemite*, Zn_2SiO_4 are also known.

Extraction

The chief ore employed for the extraction of zinc is the sulphide, which is concentrated by froth floatation process. The carbonate ore requires no enrichment. The concentrated sulphide ore is roasted on a sintering machine to give an oxide sinter. The sulphur dioxide produced is utilized for manufacture of sulphuric acid.

$$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$$
$$ZnCO_3 \rightarrow ZnO + CO_2$$

The oxide is then made into brickettes with coke and clay and heated by producer gas in vertical retorts at 1673 K. Zinc, boiling point 1183 K, distills off and is collected by rapid chilling. The crude metal is further purified by distillation or electrolytically.

Zinc is largely used for protecting iron from rusting (galvanisation and electro-galvanisation). It is also used in large quantities in batteries, and as a constituent of many alloys, e.g., brass (Cu 60%, Zn 40%) and german silver (Cu 25- 30%, Zn 25 - 30 %, Ni 40 - 50 %).

9.6.6 Mercury

Occurrence

Mercury (1×10^{-5} % of the earth's crust) is sometimes found native in rocks. The most important ore is *cinnabar* (HgS).

Extraction

The extraction of mercury is fairly simple. The ore is roasted in air above 773 K, and the mercury vapour distills over and is condensed:

$$HgS + O_2 \rightarrow Hg + SO_2$$

The richer ore and flue dust from furnaces are mixed with quicklime and distilled in iron retorts.

$$4HgS + 4CaO \rightarrow 4Hg + CaSO_4 + 3CaS$$

Commercial mercury is impure and contains a scum of oxidized metals such as zinc, cadmium, lead and copper. It can be purified by dropping slowly through dilute nitric acid, which contains a little mercury(I) nitrate. The metallic impurities displace mercury from the nitrate and go into solution.

$$Zn + Hg_2^{2+} \rightarrow 2Hg + Zn^{2+}$$

Further purification of mercury is carried out by distillation under reduced pressure.

Amalgam is an alloy of a metal with mercury. Sodium amalgam is used as a reducing agent. An amalgam of tin is used for coating mirror and a mercury-silver-tin alloy is employed for dental filling. Other uses of mercury include the production of mercury drugs and detonators. It is used in thermometers, barometers, button cells vacuum pumps and in fluorescent lamps.

9.7 SOME IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

9.7.1 Oxides and oxometal ion

These oxides are generally formed from the reaction of metal with oxygen at high temperatures. All the metals except scandium form MO oxides which are ionic. The highest oxidation number in the oxides, coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7. Beyond group 7, no higher oxides of iron above Fe_2O_3 are known. Besides the oxides, the oxocations, stabilise V^V as VO_2^+, V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+}.

As the oxidation number of a metal increases, ionic character decreases. In the case of Mn, Mn_2O_7 is a covalent green oil. Even CrO_3 and V_2O_5 have low melting point. In these higher oxides, the acidic character is predominant. Thus, Mn_2O_7 gives $HMnO_4$ and CrO_3 gives H_2CrO_4 and $H_2Cr_2O_7$. V_2O_5 is, however, amphoteric though mainly acidic and it gives VO_4^{3-} as well as VO_2^+ salts. In vanadium there is gradual change from the basic V_2O_3 to less basic V_2O_4 which dissolves in acids to give VO^{2+} salts. The well-characterised CrO is basic but Cr_2O_3 is amphoteric.

Potassium dichromate, $K_2Cr_2O_7$

Potassium dichromate is a very important chemical used in leather industry and as an oxidant for preparation of many azo compounds. Dichromates are generally prepared from *chromates*, which in turn are obtained by the fusion of *chromite* ore ($FeCr_2O_4$) with sodium or potassium carbonate in free access of air. The reaction with sodium carbonate occurs as follows:

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \rightarrow 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2$$

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7.2H_2O$ can be crystallised.

$$2\,Na_2CrO_4 + 2\,H^+ \rightarrow Na_2Cr_2O_7 + 2\,Na^+ + H_2O$$

Sodium dichromate is more soluble than potassium dichromate. The latter is prepared by treating the solution of sodium dichromate with potassium chloride.

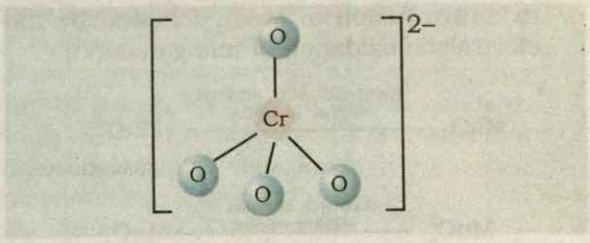
$$Na_2Cr_2O_7 + 2\,KCl \rightarrow K_2Cr_2O_7 + 2\,NaCl$$

Orange crystals of potassium dichromate crystallise out. The chromates and dichromates are interconvertable in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

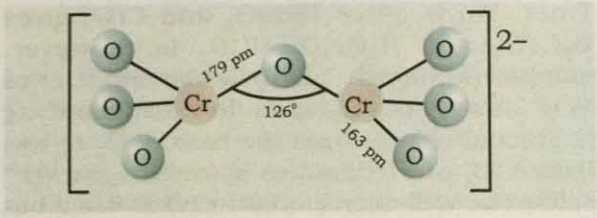
$$2\,CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

$$Cr_2O_7^{2-} + 2\,OH^- \rightarrow 2\,CrO_4^{2-} + H_2O$$

The structures of chromate ion CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$ are shown here. Whereas the chromate ion is tetrahedral, the dichromate ion consists of two tetrahedra sharing one corner with Cr-O-Cr bond angle of 126°.



Chromate ion.



Dichromate ion.

Sodium and potassium dichromates are strong oxidizing agents; the sodium salt has a greater solubility in water and is extensively used as an oxidizing agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidizing action can be represented as follows:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad (E^\ominus = 1.33\ V)$$

Thus, acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:

$$6\ I^- \rightarrow 3\ I_2 + 6\ e^-$$
$$3\ H_2S \rightarrow 6\ H^+ + 3\ S + 6\ e^-$$
$$3\ Sn^{2+} \rightarrow 3\ Sn^{4+} + 6\ e^-$$
$$6\ Fe^{2+} \rightarrow 6\ Fe^{3+} + 6\ e^-$$

The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, e.g.,

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ Fe^{2+} \rightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$$

Potassium permanganate, $KMnO_4$

(i) Potassium permanganate is prepared by fusion of MnO_2, with an alkali metal hydroxide and an oxidizing agent like KNO_3. This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

(ii) Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate(VI).

$$MnO_2 \xrightarrow[\text{with air or } KNO_3]{\text{fused with KOH, oxidised}} \underset{\text{manganate}}{MnO_4^{2-}}$$

$$\underset{\text{manganate}}{MnO_4^{2-}} \xrightarrow[\text{alkaline solution}]{\text{electrolytic oxidation in}} \underset{\text{permanganate}}{MnO_4^-}$$

Potassium permanganate is a strong oxidizing agent, both in alkaline and acidic medium. The relevant half-reactions are:

Alkaline solution: $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$ ($E^\ominus = 1.23$ V)

Acidic solution: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ ($E^\ominus = 1.515$ V)

Alkaline permanganate oxidises iodide to iodate

$$I^- + 3\ H_2O \rightarrow IO_3^- + 6\ H^+ + 6\ e^-$$

To provide the acidic medium, sulphuric acid is used instead of hydrochloric acid as the latter is oxidized to chlorine. Acidified permanganate oxidizes oxalates to carbon dioxide, iron(II) salt to iron(III), nitrites to nitrates, and liberates iodine from potassium iodide:

$$5 \begin{vmatrix} COO^- \\ | \\ COO^- \end{vmatrix} \rightarrow 10\ CO_2 + 10\ e^-$$

$$5\ Fe^{2+} \rightarrow 5\ Fe^{3+} + 5\ e^-$$
$$5\ NO_2^- + 5\ H_2O \rightarrow 5\ NO_3^- + 10\ H^+ + 10\ e^-$$
$$10\ I^- \rightarrow 5\ I_2 + 10\ e^-$$

The full ionic equation is obtained by adding the half-reaction for permanganate to the half-reaction for the reducing agent, balancing where necessary.

Potassium permanganate is used as an oxidant both in the laboratory and in industry. It is an important volumetric reagent. Its uses as a bleaching agent for wool, cotton, silk, and other textiles and for the decolourisation of oils are dependent on its oxidizing power.

9.7.2 The Halides

The transition metals react with halogens at elevated temperatures to form halides. The reactivity of halogens decreases in the order : $F_2 > Cl_2 > Br_2 > I_2$. Metals are usually oxidized to their highest oxidation states to form fluorides. The lower oxidation states are stabilised in iodides. Bonding in fluorides is usually ionic. But the ionic character decreases in chlorides, bromides and iodides with increasing mass of halogen. A few interesting halides, such as those of silver and mercury, are discussed here.

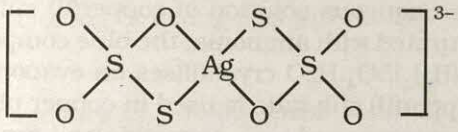
Silver halides

All the halides of silver(I) are known. The fluoride is soluble whereas the chloride, bromide and iodide are insoluble in water. Silver fluoride may

be prepared by the action of hydrofluoric acid on silver(I) oxide. The white chloride and yellow bromide and iodide are most conveniently made by double decomposition:

$$Ag^+(aq) + X^-(aq) \rightarrow AgX(s) \quad (X = Cl, Br \text{ or } I)$$

The chloride and bromide are soluble in ammonia (the chloride very readily) to give a solution containing the linear complex ion, $[Ag(NH_3)_2]^+$. Silver halides darken in light owing to photochemical decomposition, a property which is primarily responsible for their use in photography (Section 9.7.4). All the silver halides dissolve in thiosulphate and cyanide solutions giving thiosulphato and dicyano complexes of silver(I).



Dithiosulphatoargentate(I) ion

$$[\ N{\equiv}C - Ag - C{\equiv}N\ ]^-$$

Dicyanoargentate(I) ion

Silver chloride is used in photography chiefly for printing paper and lantern slides, the bromide is used in large quantities for the production of photographic films and plates and the iodide chiefly for the production of colloidal emulsion plates in photography.

Mercury halides

Mercury forms halides in the two oxidation states, +1 and +2.

Mercury(I) halides

All the mercury(I) halides are known. The most common among these is white mercury(I) chloride or *calomel* (Hg_2Cl_2). It is prepared by heating a mixture of mercury(II) chloride and mercury:

$$HgCl_2 + Hg \rightarrow Hg_2Cl_2$$

The calomel sublimes along with mercury(II) chloride. The latter is removed by extracting the mixture with water which removes the sparingly soluble Hg(II) chloride.

It can also be obtained by the reduction of mercury(II) chloride by a reducing agent, e.g., tin(II) chloride in limiting quantity:

$$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$$

When heated, mercury(I) chloride decomposes into mercury(II) chloride and mercury.

The action of aqueous ammonia on the solid mercury(I) chloride gives a mixture of black finely divided mercury and white mercury aminochloride, i.e., disproportionation occurs:

$$Hg_2Cl_2 + 2NH_3 \rightarrow Hg + Hg(NH_2)Cl + NH_4Cl$$

Mercury(I) chloride is used in calomel electrodes.

Mercury(II) halides

The commonest among them is mercury(II) chloride, which is known as *corrosive sublimate*. It may be prepared by heating the metal in chlorine gas or heating mercury(II) sulphate with common salt and manganese dioxide, when mercury(II) chloride sublimes off:

$$HgSO_4 + 2NaCl \rightarrow HgCl_2 + Na_2SO_4$$

Manganese dioxide prevents the formation of mercury(I) chloride.

Mercury(II) chloride forms white crystalline mass but from aqueous solution it crystallises in to colourless needles. It is a covalent compound, sparingly soluble in water, the solubility being increased by the addition of chloride ions, when a soluble tetrachloromercurate (II) complex ion is formed.

$$HgCl_2 + 2Cl^- \rightarrow [HgCl_4]^{2-}$$

Mercury(II) chloride reacts with aqueous ammonia to form a white precipitate of mercury aminochloride, (i.e., *infusible white precipitate*).

$$HgCl_2 + 2NH_3(aq) \rightarrow Hg(NH_2)Cl + NH_4Cl$$

The infusible white precipitate decomposes without melting on heating. Gaseous ammonia or ammonium chloride on reaction with mercury(II) chloride produces a *fusible white precipitate* of diamminemercury(II) chloride.

$$HgCl_2 + 2NH_3 \rightarrow Hg(NH_3)_2Cl_2$$

Mercury(II) chloride solution is reduced by many reducing agents, e.g., formaldehyde, tin(II) chloride, sulphur dioxide, etc., precipitating white mercury(I) chloride first, which with excess of reducing agent turns black owing to the formation of metallic mercury.

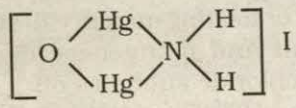
$$2HgCl_2 + SnCl_2 \rightarrow \underset{\text{white}}{Hg_2Cl_2} + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \rightarrow \underset{\text{black}}{2Hg} + SnCl_4$$

Mercury(II) iodide is obtained as a scarlet precipitate on addition of potassium iodide to a solution of mercury(II) chloride. It can also be obtained by grinding mercury with appropriate amount of iodine. Mercury(II) iodide, although sparingly soluble in water, dissolves readily in a solution of potassium iodide due to the formation of iodo complex, e.g.,

$$HgI_2 + 2KI \rightarrow \underset{\text{potassium tetraiodomercurate(II)}}{K_2[HgI_4]}$$

The tetraiodo complex forms light yellow crystals, $K_2[HgI_4].2H_2O$, freely soluble in water and alcohol. The complex dissolves in potassium hydroxide solution to give Nessler's reagent which forms a brown precipitate or colouration with ammonia owing to the formation of the iodide of Millon's base, $Hg_2NI.H_2O$ having the following structure.



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Mercury(II) iodide finds application for the treatment of skin infection and for the preparation of Nessler's reagent.

9.7.3 Salts of Oxoacids

The higher elements of first transition series have at least one stable oxidation state each of which furnishes stable hydrated cations and forms salts of oxoacids. Metals of the second and third series form few simple cations and hence few oxosalts. Also the large number of complexes which exist for the first transition series are almost entirely absent with the heavier metals. Let us study here a few of the oxosalts.

Copper sulphate

The most common oxosalt of copper(II) is *blue vitriol*, $CuSO_4.5H_2O$. It is prepared industrially by blowing a current of air through copper scrap and dilute sulphuric acid.

$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O$$

The crude copper(II) sulphate solution obtained contains iron(II) sulphate as impurity. Dilute nitric acid is added to oxidise iron(II) to iron(III) sulphate, which remains in solution after crystallization. The pentahydrate, $CuSO_4.5H_2O$, crystallizes out.

Crystalline copper sulphate is readily soluble in water. The salt, $CuSO_4.5H_2O$ is insoluble in alcohol and is precipitated on adding alcohol to the aqueous solution. When heated slowly, the pentahydrate decomposes in the following stages:

$$CuSO_4.5H_2O \xrightarrow{305\,K} CuSO_4.3H_2O \xrightarrow{373\,K}$$

$$CuSO_4.H_2O \xrightarrow{573\,K} CuSO_4 \xrightarrow{673\,K} CuO + SO_3$$

The crystalline copper(II) sulphate, $CuSO_4.5H_2O$, has the structure in which four water molecules are coordinated to the central copper cation at the centre of a square but the fifth water molecule is held by hydrogen bonds between a sulphate ion and a coordinated water molecule. The fifth hydrogen bonded water molecule is deeply embedded in the crystal lattice and hence not easily removed.

Copper(II) sulphate forms well-defined crystalline double salts with sulphates of strongly electropositive metals which generally correspond to the type $M^1_2SO_4.CuSO_4.6H_2O$ and are greenish blue in colour, $(NH_4)_2SO_4.CuSO_4.6H_2O$. These double salts are isomorphous with the double salts of bivalent metals, Fe, Co, Ni. The aqueous solution of copper(II) sulphate is slowly hydrolysed forming basic copper sulphate.

If an aqueous solution of copper(II) sulphate is saturated with ammonia, the blue compound, $[Cu(NH_3)_4]SO_4.H_2O$ crystallises on evaporation.

Copper(II) sulphate is used in copper plating, electrotyping, and as a germicide and fungicide [Bordeaux mixture is $CuSO_4$ and $Ca(OH)_2$].

Silver nitrate, $AgNO_3$

Silver nitrate is technically the most important of silver compounds. It is prepared by dissolving metallic silver in dilute nitric acid. From solution it crystallizes as large rhombic plates, m.p. 482 K. It is not hygroscopic and is very soluble in water. The solubility increases with increasing temperature (e.g., 100 g of water dissolves 400g at 323 K and 910 g at 373 K). Aqueous solutions are susceptible to decomposition by light. When heated it decomposes in two stages:

$$2\,AgNO_3 \xrightarrow{723\,K} 2\,AgNO_2 + O_2 \xrightarrow{980\,K} Ag + NO_2$$

Silver nitrate is also decomposed by organic matter, such as glucose, paper, skin and cork. It has also a caustic and destructive effect on organic tissues.

Large quantities of silver nitrate are used in the production of light sensitive plates, films and papers. In the laboratories it is extensively used as a group reagent for the detection of halide ions. In small doses, silver nitrate is used as a medicine in nervous diseases. A solution of silver nitrate is used in marking linen. Silver nitrate is also used in silvering of mirror.

9.7.4 Photography

A photographic plate or film is essentially a layer of an emulsion of a silver halide (most frequently silver bromide) in gelatine and water applied to

a glass or celluloid sheet. The emulsion is prepared by mixing a solution of silver nitrate, gelatine and potassium bromide in hot water (a little potassium iodide is usually present). The silver bromide with a little iodide is precipated and the warm mixture is allowed to stand for some time. The process is called *ripening* and makes the emulsion more sensitive to light. The emulsion is allowed to cool and set and then washed with water to remove soluble material. It is then melted and applied to glass or celluloid sheet and dried. After the plate or film is ready for use, the following processes are undertaken for photography in stages: 1) Exposure 2) Developing 3) Fixing and 4) Printing.

Exposure

The exposure of photographic plate or film to the object results in the decomposition of silver halides coated on the film; submicroscopic particles of silver are formed and the halogen combines with the gelatin.

Developing

The film is now developed by adding an organic reducing agent when more silver bromide is reduced, the rate of reduction depending upon the intensity of illumination during the exposure period. Thus, parts of the film which were most strongly illuminated become the darkest. It is this intensification of the latent image first formed that permits the use of short exposure times and causes silver halide to occupy their unique position in photography.

Fixing

The film is now washed with aqueous solution of sodium thiosulphate which removes the unchanged silver halide as a complex, $[Ag(S_2O_3)_2]^{3-}$. The negative is now ready and can be handled in day-light.

In order to make print from the negative, light is allowed to pass through it on to silver bromide-containing photographic paper which is then treated in a similar way as the negative. The negative image is thus reversed.

THE INNER TRANSITION ELEMENTS (*f*-Block)

The *f*-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium). Because lanthanum closely resembles the lanthanoids, it is usually included in any discussion of the lanthanoids for which the general symbol Ln is often used. Similarly, a discussion of the actinoids includes actinium besides the fourteen elements constituting the series. The lanthanoids resemble one another more closely than do the members of ordinary transition elements in any series. They have only one stable oxidation state and their chemistry provides an excellent opportunity to examine the effect of small changes in size and nuclear charge along a series of otherwise similar elements. The chemistry of the actinoids is, on the other hand, much more complicated and the complication arises partly owing to the occurrence of wide range of oxidation states in these elements and partly because their radioactivity creates special problems in their study.The two series will be considered separately here.

9.8 THE LANTHANOIDS

The names, symbols, electronic configurations of atomic and some ionic states and atomic and ionic radii of lanthanum and lanthanoids (for which the general symbol Ln is used) are assembled in Table 9.6.

Electronic configuration

It may be noted (Table 9.6) that atoms of these elements have electronic configuration with $6s^2$ common but with variable occupancy of $4f$ level. However, the electronic configurations of all the tripositive ions (the most stable oxidation state of all the lanthanoids) are of the form $4f^n$ (n = 1 to 14 with increasing atomic number).

Atomic and ionic sizes

The overall decrease in atomic and ionic radii from lanthanum to lutetium (the **lanthanoid contraction**) is a unique feature in the chemistry of the lanthanoids. It has (as we have already seen) far reaching consequences in the chemistry of the third transition series of the elements.The decrease in atomic radii (derived from the structures of metals) is not quite regular as it is regular in M^{3+} ions (Fig. 9.6). This contraction is, of course, similar to that observed in an ordinary transition series and is attributed to the same cause, the imperfect shielding of one electron by another in the same sub-shell. However, the shielding of one $4f$ electron by

another is less than that of one *d* electron by another and with the increase in nuclear charge along the series, there is fairly regular decrease in the sizes with increasing atomic number.

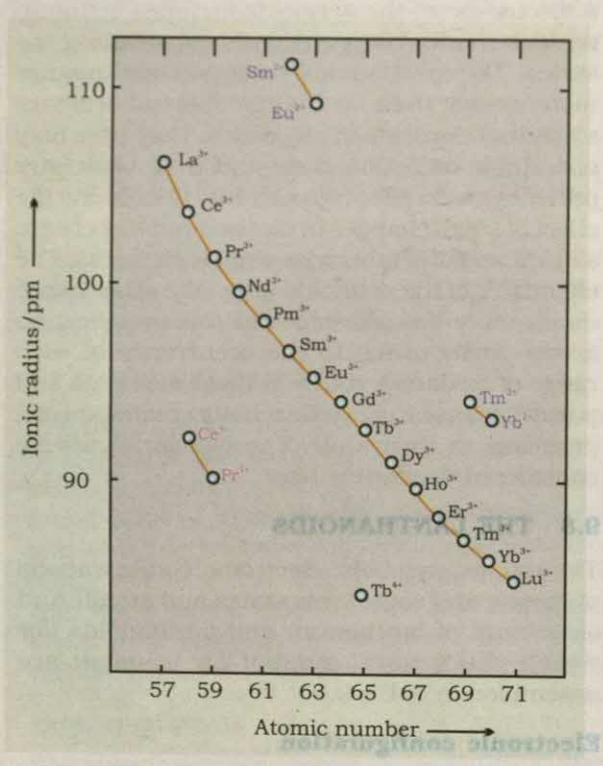


Fig. 9.6 *Trends in ionic radii of trivalent lanthanoids.*

The cumulative effect of the contraction of the lanthanoid series, known as *lanthanoid contraction*, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

Colour and Paramagnetism

Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of *f* electrons. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so. However, absorption bands are narrow, probably because of the excitation within *f* level.

The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism rises to maximum in neodymium.

Ionization enthalpies

The first ionization enthalpies of the lanthanoids are around 600 kJ mol^{-1}, the second about 1200 kJ mol^{-1} comparable with those of calcium. A detailed discussion of the variation of the third ionisation enthalpies indicates that the exchange

Table 9.6 Electronic conifigurations and radii of lanthanum and lanthanoids

Atomic Number	Name	Symbol	Electronic configuration*				Radii/pm	
			Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}	Ln	Ln^{3+}
57	Lanthanum	La	$5d^16s^2$	$5d^1$	$4f^0$		187	106
58	Cerium	Ce	$4f^15d^16s^2$	$4f^2$	$4f^1$	$4f^0$	183	103
59	Praseodymium	Pr	$4f^36s^2$	$4f^3$	$4f^2$	$4f^1$	182	101
60	Neodymium	Nd	$4f^46s^2$	$4f^4$	$4f^3$	$4f^2$	181	99
61	Promethium	Pm	$4f^56s^2$	$4f^5$	$4f^4$		181	98
62	Samarium	Sm	$4f^66s^2$	$4f^6$	$4f^5$		180	96
63	Europium	Eu	$4f^76s^2$	$4f^7$	$4f^6$		199	95
64	Gadolinium	Gd	$4f^75d^16s^2$	$4f^75d^1$	$4f^7$		180	94
65	Terbium	Tb	$4f^96s^2$	$4f^9$	$4f^8$	$4f^7$	178	92
66	Dysprosium	Dy	$4f^{10}6s^2$	$4f^{10}$	$4f^9$	$4f^8$	177	91
67	Holmium	Ho	$4f^{11}6s^2$	$4f^{11}$	$4f^{10}$		176	89
68	Erbium	Er	$4f^{12}6s^2$	$4f^{12}$	$4f^{11}$		175	88
69	Thulium	Tm	$4f^{13}6s^2$	$4f^{13}$	$4f^{12}$		174	87
70	Ytterbium	Yb	$4f^{14}6s^2$	$4f^{14}$	$4f^{13}$		173	86
71	Lutetium	Lu	$4f^{14}5d^16s^2$	$4f^{14}5d^1$	$4f^{14}$	–	–	–

*Only electrons outside [Xe] core are indicated

enthalpy considerations (as in 3*d* subshell of the first transition series), appear to impart a certain degree of stability to empty, half-filled and completely filled *f* level. This is indicated from the abnormally low value of the third ionization enthalpy of lanthanum, gadolinium and lutetium.

Oxidation states

In the lanthanoids, La^{3+} and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity (as in ionization enthalpies) arises mainly from the extra stability of empty, half-filled or filled *f* subshell. Thus, the formation of Ce^{IV} is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The $E^{\ominus}$ value for Ce^{4+}/Ce^{3+} is +1.74 V to oxidize water but the reaction rate is very slow, hence Ce(IV) is a good analytical reagent. Pr, Nd, Tb. and Dy also exhibit +4 state but only in oxides, MO_2. Eu^{2+} is formed by losing the two *s* electrons and its f^7 configuration accounts for the formation of this ion. However, Eu^{2+} is a strong reducing agent changing to the common +3 state. Similarly Yb^{2+} which has f^{14} configuration is a reductant. Tb^{IV} has a half-filled *f* subshell and is an oxidant. The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.

Properties and Uses

All the lanthanoids are silvery white soft metals and tarnish rapidly in air – the hardness increases with increasing atomic number, samarium being steel hard. Their melting points range between 1000 to 1200 K but samarium melts at 1623 K. They have typical metallic structure and are good conductors of heat and electricity. Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.

In their chemical behaviour, in general, the earlier members of the series are quite reactive similar to calcium but, with increasing atomic number, they behave more like aluminium. Values for $E^{\ominus}$ for the half-reaction:

$$Ln^{3+}(aq) + 3e^- \rightarrow Ln(s)$$

are in the range of –2.2 to –2.4 V except for Ln = Eu for which the value is –2.0 V. This is, of course, a small variation. The metals combine with hydrogen when gently heated in the gas. The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon. They liberate hydrogen from dilute acids and burn in halogens to form halides. They form oxides and hydroxides, M_2O_3 and $M(OH)_3$. The hydroxides are definite compounds, not just hydrated oxides, basic like alkaline earth metal oxides and hydroxides. Their general reactions are given in Fig. 9.7.

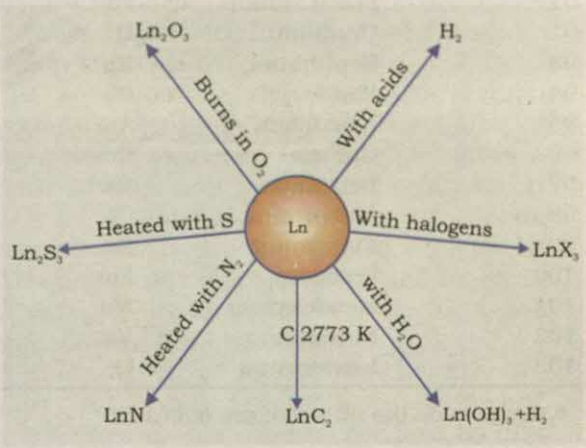


Fig 9.7 *Chemical reactions of the lanthanoids.*

The best single use of the lanthanoids is for the production of alloy steels for plates and pipes. A well-known alloy is *mischmetall* which consists of a lanthanoid metal (~ 95%) and iron (~5%) and traces of S, C, Ca and Al. A good deal of mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint. Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking. Some individual Ln oxides are used as *phosphors* in television screens and similar fluorescing surfaces.

9.9 THE ACTINOIDS

The actinoids include the fourteen elements from Th to Lr. The names, symbols, and some properties of these elements are given in Table 9.7.

Although the naturally occurring elements and the earlier members have relatively long half-lives, the later members have values ranging from days to 3 minutes for lawrencium (Z = 103). This, and high radioactivity renders their study more difficult.

Electronic configuration

All the actinoids are believed to have the electron configuration of $7s^2$ and variable

Table 9.7 Some properties of actinium and actinoids

Atomic Number	Name	Symbol	Electronic conifiguration*			Radii/pm	
			M	M^{3+}	M^{4+}	M^{3+}	M^{4+}
89	Actinium	Ac	$6d^1 7s^2$	$5f^0$		111	
90	Thorium	Th	$6d^2 7s^2$	$5f^1$	$5f^0$		99
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$	$5f^1$		96
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^6 7s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^7 7s^2$	$5f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$	$5f^6$	99	88
97	Berkelium	Bk	$5f^9 7s^2$	$5f^8$	$5f^7$	98	87
98	Californium	Cf	$5f^{10} 7s^2$	$5f^9$	$5f^8$	98	86
99	Einstenium	Es	$5f^{11} 7s^2$	$5f^{10}$	$5f^9$	–	–
100	Fermium	Fm	$5f^{12} 7s^2$	$5f^{11}$	$5f^{10}$	–	–
101	Mendelevium	Md	$5f^{13} 7s^2$	$5f^{12}$	$5f^{11}$	–	–
102	Nobelium	No	$5f^{14} 7s^2$	$5f^{13}$	$5f^{12}$	–	–
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$	$5f^{13}$	–	–

*Only outside the [Rn] core are indicated

occupancy of the *5f* and *6d* subshells. The fourteen electrons are formally added to *5f*, though not in thorium ($Z = 90$) but onwards from it and the *5f* is complete at element 103. The irregularities in the electronic configuration of the actinoids, like those in the lanthanoids are related to the stabilities of the f^0, f^7, and f^{14} occupancies of the *5f* orbitals. Thus, the configurations of Am and Cm are [Rn] $5f^7 7s^2$ and [Rn]$5f^7 6d^1 7s^2$. Although the *5f* orbitals resemble the *4f* in their angular part of the wave-function, unlike *d* orbitals which are buried and hence their electrons are rarely ionized or shared, the electrons in *5f* orbitals can and do participate in bonding to a far greater extent.

Oxidation states

There is a greater range of oxidation states, which is in part attributed to the fact that the *5f*, *6d* and *7s* levels are of comparable energies. The known oxidation states of actinoids are listed in Table 9.8.

We may infer from these that the actinoids show in general +3 oxidation state. The elements in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements (Table 9.8). The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse. Because the distribution of oxidation states among the actinoids is so uneven and so different for the earlier and later elements, it is unsatisfactory to review their chemistry in terms of oxidation states.

Table 9.8 Oxidation states of actinium and actinoids

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3		3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

Magnetic properties

The magnetic properties of the actinoids are more complex than those of the lanthanoids. Although the variation in the magnetic susceptibility of the actinoids with the number of unpaired *5f* electrons is roughly parallel to the corresponding results for the lanthanoids, the latter have higher values.

Ionic sizes

The general trend observed in lanthanoids is observable in the actinoids as well. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the *actinoid contraction* (like lanthanoid contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by *5f* electrons.

Ionisation enthalpy

It is evident from the behaviour of the actinoids that the ionization enthalpies of the early actinoids, though not accurately known, but are lower than for the early lanthaniods. This is quite reasonable since it is to be expected that when *5f* orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons, and the *5f* electrons, will therefore, be more effectively shielded from the nuclear charge than are the *4f* electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids as far as Np but only for Ce in the lanthanoids.

Physical and chemical reactivity

The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is mirrored by irregularities in metallic radii which are far greater than are found in lanthanoids.

The actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non-metals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action.

A comparison of the actinoids with the lanthanoids with respect to different characteristics as discussed above, reveals that behaviour like that of the lanthanoids is not evident until the second half of the actinoid series. However, even the early actinoids resemble the lanthanoids in showing close similarities with each other and in gradual variation in properties which do not entail a change in oxidation state.

SUMMARY

The *d*-block consisting of Groups 3-12 occupies the large middle section of the Periodic table. In these elements the inner *d* orbitals are progressively filled. The *f*-block is placed outside at the bottom of the Periodic table and in the elements of this block, *4f* and *5f* orbitals are progressively filled.

Corresponding to the filling of *3d*, *4d*, and *5d* subshells, three series of transition elements are well recognised. All the transition elements exhibit typical metallic properties such as-high tensile strength, ductility, malleability, thermal and electrical conductivity and metallic character. Their melting and boiling points are high which are attributed to the involvement of $(n\text{-}1)d$ electrons resulting into strong interatomic bonding. In many of these properties, the maxima occurs at about middle of each series which indicates that one unpaired electron per *d* orbital is particularly favourable configuration for strong interatomic interaction.

Successive ionisation enthalpies do not increase as steeply as in the main group elements with increasing atomic number. Hence, the loss of variable number of electrons from $(n\text{-}1)d$ orbitals is not energetically prohibitive. The involvement of $(n\text{-}1)d$ electrons in the behaviour

of transition elements impart certain distinct characteristics to these elements. Thus, in addition to variable oxidation states, they exhibit paramagnetic behaviour, catalytic properties and tendency for the formation of coloured ions, interstitial compounds and complexes.

The transition elements vary widely in their chemical behaviour. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble'. Of the first series, with the exception of copper, all the metals are relatively reactive.

Occurrence and principles of extraction of iron, copper, silver, zinc and mercury have been considered in some detail. These metals find variety of uses. Iron in the form of steel is by far the most important metal of the modern world. The modern methods of steel making are oxygen top-blowing, electric arc and high-frequency induction processes.

The transition metals react with a number of non-metals like oxygen, nitrogen, sulphur and halogens to form binary compounds. The first series transition metal oxides are generally formed from the reaction of metals with oxygen at high temperatures. These oxides dissolve in acids and bases to form oxometallic salts. Potassium dichromate and potassium permanganate are common examples. Potassium dichromate is prepared from the chromite ore by fusion with alkali in presence of air and acidifying the extract. Pyrolusite ore (MnO_2) is used for the preparation of potassium permanganate. Both the dichromate and the permanganate are strong oxidising agents. Among the halides, chlorides of silver and mercury are obtained by the action of chlorine on the respective metal. Their reactions with ammonia are of some interest. Silver halides are especially important for their role in photography. Of the salts of oxoacids, copper sulphate and silver nitrate are quite familiar. Silver nitrate is mostly used for the preparation of light sensitive plates, films and paper to be used in photography. The processes undertaken for photography include exposure, developing, fixing and printing.

The two series of inner transition elements, lanthanoids and actinoids constitute the *f* - block of the periodic table. With the successive filling of an inner subshell, *4f*, there is a gradual decrease in the atomic and ionic sizes of these metals along the series (lanthanoid contraction) which has far reaching consequences in the chemistry of the elements succeeding them. Lanthanum and all the lanthanoids are rather soft white metals. They react easily with water to give solutions giving +3 ions. The principal oxidation state is +3, although +4 and +2 oxidation states are also exhibited by some occasionally. The chemistry of the actinoids is more complex in view of their ability to exist in different oxidation states. Furthermore, many of the actinoid elements are radioactive which makes the study of these elements rather difficult. When compared with the lanthanoids, in the first half of the series there is much wider variation in chemical properties than found among the lanthanoids. In the second half of the series, however, the tripositive state is the most stable for nearly all the elements and similarities to the lanthanoids are much more apparent.

EXERCISES

9.1 Write down the electronic configurations of:
(a) Cr^{3+} (b) Cu^{+} (c) Co^{2+} (d) Mn^{2+}
(e) Pm^{3+} (f) Ce^{4+} (g) Lu^{2+} (h) Th^{4+}

9.2 Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?

9.3 Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?

9.4 To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with example.

9.5 What may be the stable oxidation state of the transition element with the following *d* electron configurations in the ground state of their atoms : $3d^3$, $3d^5$, $3d^8$, and $3d^4$?

9.6 Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

9.7 What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

9.8 What are the characteristics of the transition elements and why are they called transition elements? Which of the *d*-block elements may not be regarded as the transition elements?

9.9 In what way is the electronic configuration of the transition elements different from that of the non-transition elements?

9.10 What are the different oxidation states exhibited by the lanthanoids?

9.11 Explain giving reason:
(a) Transition metals and many of their compounds show paramagnetic behavior.
(b) The enthalpies of atomisation of the transition metals are high.
(c) The transition metals generally form coloured compounds.
(d) Transition metals and their many compounds act as good catalyst.

9.12 What are interstitial compounds? Why are such compounds well known for transition metals?

9.13 How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.

9.14 Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?

9.15 Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:
(a) iodide (b) iron(II) solution (c) H_2S

9.16 Describe the preparation of potassium permanganate. How does the acidified permanganate solution reacts with a) iron(II) ions b) SO_2 c) oxalic acid? Write the ionic equations for the reactions.

9.17 For M^{2+}/M and M^{3+}/M^{2+} systems the $E^{\ominus}$ values for some metals are as follows:

Cr^{2+}/Cr	– 0.9 V	Cr^{3+}/Cr^{2+}	–0.4 V
Mn^{2+}/Mn	– 1.2 V	Mn^{3+}/Mn^{2+}	+1.5 V
Fe^{2+}/Fe	– 0.4 V	Fe^{3+}/Fe^{2+}	+0.8 V

Use this data to comment upon:
(a) The stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} or Mn^{3+}
(b) The ease with which iron can be oxidised as compared to the similar process for either chromium or manganese metal.

9.18 Predict which of the following will be coloured in aqueous solution?
Ti^{3+}, V^{3+}, Cu^{+}, Sc^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+} and MnO_4^-.
Give reason for each.

9.19 Compare the stability of +2 oxidation state for the elements of the first transition series.

9.20 Name chief ores of iron. How is the pig iron converted into steel? Describe any one method of steel making in detail.

9.21 Name the chief ore of copper and of zinc. Describe the principle of extraction of these metals from the respective ore.

9.22 Describe the chemistry of the three stages of photography, i.e., exposure, developing, and fixing.

9.23 Compare the chemistry of actinoids with that of the lanthanoids with special reference to:
(a) electronic configuration
(b) oxidation state
(c) atomic and ionic sizes and
(d) chemical reactivity.

9.24 How would you account for the following:
(a) Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III) is strongly oxidising.
(b) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.

(c) The d^1 configuration is very unstable in ions.

9.25 What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.

9.26 Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

9.27 Calculate the number of unpaired electrons in following gaseous ions: Mn^{3+}, Cr^{3+}, V^{3+}, and Ti^{3+}. Which one of these is the most stable in aqueous solution?

9.28 Give example and suggest reasons for the following features of the transition metal chemistry:

(a) The lowest oxide of a transition metal is basic, the highest is acidic.

(b) A transition metal exhibits higher oxidation states in oxides and fluorides.

(c) The highest oxidation state is exhibited in oxoanions of a metal.

9.29 Indicate the steps in the preparation of:

(a) $K_2Cr_2O_7$ from chromite ore

(b) $KMnO_4$ from pyrolusite ore

(c) Copper sulphate from metallic copper

(d) Calomel from corrosive sublimate.

9.30 What happens when aqueous ammonia reacts with:

(a) silver chloride

(b) mercury (I) chloride

(c) mercury (II) chloride?

9.31 Describe two uses of each of the following:

(a) Copper sulphate (b) Silver nitrate (c) Silver bromide.

9.32 What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.

9.33 What are inner transition elements? Which of the following atomic numbers belong to the inner transition elements : 29, 59, 74, 95, 102, 104.

9.34 The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

9.35 Which is the last element in the series of the actinoids? Write the electronic configuration of these elements. Comment on the possible oxidation state of this element.

9.36 Use Hund's rule to derive the electronic configuration of Ce^{3+} ion, and calculate its magnetic moment on the basis of 'spin-only' formula.

9.37 Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configuration of these elements.

9.38 Compare the chemistry of the actinoids with that of lanthanoids with reference to: (i) electronic configuration (ii) oxidation states, and (iii) chemical reactivity.

9.39 What is lanthanoid contraction? What is its effect on the chemistry of the elements which follow the lanthanoids?

9.40 Write the electronic configurations of the elements with the atomic numbers 61, 91, 101, and 109.

UNIT 10

COORDINATION COMPOUNDS AND ORGANOMETALLICS

OBJECTIVES

After studying this Unit, you will be able to:

- understand the postulates of Werner's theory of coordination compounds.
- know the meaning of the terms; coordination entity (complex), central atom, ligand, coordination number, coordination polyhedron, oxidation number, denticity and chelation.
- learn the rules of nomenclature of coordination compounds.
- write the formulae and names of mononuclear coordination compounds.
- understand the nature of bonding in coordination compounds in terms of the Valence Bond and Crystal Field theories.
- explain the stability of coordination compounds.
- define and classify organometallic compounds.
- understand the basic nature of bonding in organometallic compounds with particular reference to metal carbonyls.
- appreciate the importance and applications of coordination and organometallic compounds.

Coordination and organometallic compounds are the bedrocks of modern inorganic chemistry and chemical industry.

The chemistry of coordination compounds and organometallics is an important and challenging area of modern inorganic chemistry. The exciting field of bio-inorganic chemistry too is centered on coordination compounds present in the living systems. Developments in these areas, over the years, have: (i) led to new concepts of chemical bonding and models of molecular structure; (ii) revolutionised the chemical industry; and, (iii) provided critical insights into the functioning and structures of vital components of biological systems. Coordination compounds also find extensive applications in metallurgical processes, analytical and medicinal chemistry.

The formation of stable compounds by the interaction of species, themselves capable of independent stable existence, puzzled the chemists in the beginning. Thus, it was baffling that cobalt chloride and ammonia, both independent stable compounds should combine to form a series of new compounds (Table 10.1). Such compounds were, therefore, labelled as **complex compounds**[1]. In the modern terminology such compounds are called **coordination compounds.**

10.1 WERNER'S THEORY OF COORDINATION COMPOUNDS

The systematic study of coordination compounds was started by **Alfred Werner** whose pioneering work opened an entirely new field of investigation in inorganic chemistry. He prepared and characterized a large number of coordination compounds and studied their physical, chemical

[1] *This label though still popular with researchers and authors, should, as per the recommendation of IUPAC, be replaced by the term coordination entity. However, in this textbook the two said terms will be used synonymously.*

and isomeric behaviour by simple experimental techniques. On the basis of these studies, Werner, in 1898, propounded his theory of coordination compounds.

Table 10.1 Series of coloured compounds obtained by the interaction of aqueous $CoCl_3$ and NH_3

Compound	Colour	Name according to colour	
$CoCl_3.6NH_3$	Yellow	Luteo Complex	
$CoCl_3.5NH_3$	Purple	Purpureo Complex	
$CoCl_3.4NH_3$	Green	Praseo Complex	Isomers
$CoCl_3.4NH_3$	Violet	Violeo Complex	

The main postulates of Werner's theory are:

- metals exert two types of linkages; (i) the **primary** or ionizable links which are satisfied by negative ions and equal the oxidation state of the metal, and (ii) the **secondary** or nonionizable links which can be satisfied by neutral or negative ions/groups. The secondary linkages equal the **coordination number** of central metal atom/ion. This number is fixed for a metal.
- the ions/groups bound by the secondary linkages have characteristic spatial arrangements corresponding to different co-ordination numbers. In the modern terminology, such spatial arrangements are called **coordination polyhedra**.

On the basis of the above postulates, Werner formulated the coordination compounds, $CoCl_3.6NH_3$, $CoCl_3.5NH_3$ and $CoCl_3.4NH_3$ as: $[Co(NH_3)_6]Cl_3$, $[CoCl(NH_3)_5]Cl_2$ and $[CoCl_2(NH_3)_4]Cl$, respectively – the species within the square brackets being the **coordination entities (complexes)** and the ions outside the square brackets the **counter ions**. He further postulated that octahedral, square – planar and tetrahedral geometrical shapes are more common in coordination compounds of transition metals. Thus, $[Co(NH_3)_6]^{3+}$, $[CoCl(NH_3)_5]^{2+}$, $[CoCl_2(NH_3)_4]^{+}$ are octahedral entities, while $[Ni(CO)_4]$ and $[PtCl_4]^{2-}$ are tetrahedral and square-planar, respectively.

Alfred Werner

Alfred Werner (1866-1919) was a Swiss chemist, who, though an organic chemist by training, got interested in coordination chemistry. He prepared and characterised hundreds of coordination compounds. His theory, outlining the nature of bonding in, and structures of coordination compounds, at a time when almost nothing was known about valence, is a great landmark in the annals of inorganic chemistry. Werner was awarded the Nobel Prize in chemistry in 1913.

10.2 DEFINITIONS OF SOME IMPORTANT TERMS PERTAINING TO COORDINATION COMPOUNDS

Some important terms required for the description of a coordination compound are: **coordination entity, central atom, ligand, coordination number, coordination polyhedron, denticity, chelation and oxidation number** (of the central atom). Their definitions and meanings are described below.

Coordination Entity (Complex)

A coordination entity constitutes a central atom/ion, usually of a metal, to which are attached a fixed number of other atoms or groups each of which is called a **ligand**. It may be neutral or charged. Examples being: $[Co(NH_3)_6]^{3+}$, $[PtCl_4]^{2-}$, $[Fe(CN)_6]^{3-}$, $[NiCl_2(H_2O)_4]$.

Example 10.1
Designate the coordination entities and counter ions in the coordination compounds: $[Cr(NH_3)_6]Cl_3$; $K_4[Fe(CN)_6]$, $K_2[PtCl_4]$; $[Ni(CO)_4]$; $K_2[Ni(CN)_4]$.

Solution
The respective coordination entities are: $[Cr(NH_3)_6]^{3+}$; $[Fe(CN)_6]^{4-}$; $[PtCl_4]^{2-}$; $[Ni(CO)_4]$; $[Ni(CN)_4]^{2-}$; and the counter ions are Cl^-, K^+ K^+, (no counter ion) and K^+, respectively in the given coordination compounds.

Central atom/ion

In a coordination entity – the atom/ion to which are bound a fixed number of ligands in a definite geometrical arrangement around it, is called the **central atom** or **ion**. For example, the central atom/ion in the coordination entities: $[NiCl_2(H_2O)_4]$, $[CoCl(NH_3)_5]^{2+}$, $[Fe(CN)_6]^{3-}$ are Ni^{2+}, Co^{3+} and Fe^{3+}, respectively.

Ligands

The **ligands** are the ions or molecules bound to the central atom/ion in the coordination entity. This is better visualized as the combination of a Lewis acid (the central atom/ion) with a number of Lewis bases (ligands) (Unit 8, Class XI). The atom in the Lewis base that forms the bond to the Lewis acid (central atom/ion) is called **donor atom** (because it donates the pair of electrons required for bond formation). The central atom/ion is the **acceptor atom/ion** (because it receives the electron pairs from the ligands). Some of the common ligands in coordination compounds are: Br^-, Cl^-, CN^-, OH^-, O^{2-}, CO_3^{2-}, NO_2^-, $C_2O_4^{2-}$, NH_3, CO, H_2O, $NH_2CH_2CH_2NH_2$ (1,2- ethanediamine).

Ligands which can ligate through two different atoms present in it are called **ambidentate ligands**. Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate through either the nitrogen or the oxygen atoms to a central metal atom/ion. Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom. Such possibilities give rise to **linkage isomerism** in coordination compounds (Section 10.4.4).

Coordination Number

The **coordination number** of the central atom/ion is determined by the number of sigma bonds between the ligands and the central atom/ion. Pi-bonds, if any, between the ligating atom and the central atom/ion are not considered for the determination of coordination number. The sigma bonding electrons may be indicated by a pair of dots:, preceding the donor atom in the ligand formula as in: $[Co(:NH_3)_6]^{3+}$, $[Fe(:CN)_6]^{3-}$, $[Ni(:CO)_4]$, $[Co(:Cl_4)]^{2-}$.

Coordination Polyhedron

The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom. Fig. 10.1 shows the shapes of tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal coordination polyhedra. We have already learnt (Section 10.1) that $[Co(NH_3)_6]^{3+}$ has an octahedral geometry, while $[PtCl_4]^{2-}$ and $Ni(CO)_4$, are square planar and tetrahedral, respectively.

Oxidation number of Central Atom

The **oxidation number** of the central atom is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. Oxidation number is represented by a Roman numeral in parenthesis following the name of the coordination entity. Some examples are listed in Table 10.2.

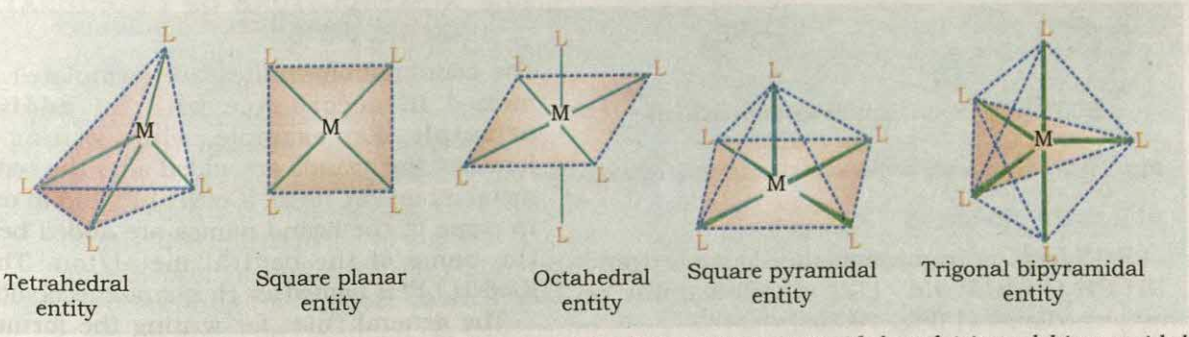


Fig. 10.1 *Shapes of tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal coordination polyhedra. M represents the central atom/ion and L, a unidentate ligand.*

Table 10.2 Examples of important terms used in describing coordination entities

Coordination entity (complex)	Ligand list	Central atom/oxidation number	Geometrical shapes
$[Co(NH_3)_6]^{3+}$	$6NH_3$	Co / (III)	Octahedral
$[NiCl_4]^{2-}$	$4Cl^-$	Ni / (II)	Tetrahedral
$[Co(CN)_5F^-]^{3-}$	$5CN^- + 1F^-$	Co / (III)	Octahedral
$[Ni(CN)_4]^{2-}$	$4CN^-$	Ni / (II)	Square-planar
$[Ni(CO)_4]$	4CO	Ni / (0)	Tetrahedral
$[Ni(H_2O)_6]^{2+}$	$6H_2O$	Ni / (II)	Octahedral

Denticity and Chelation

When coordination of more than one sigma-electron pair donor group from the ligand to the same central atom/ion takes place, it is called **chelation**, and the ligand a **chelating ligand**. The number of such ligating groups indicate the **denticity** of the ligand. For example: unidentate, didentate, tridentate, tetradentate, etc. In Fig. 10.2 are shown some of the common chelating ligands.

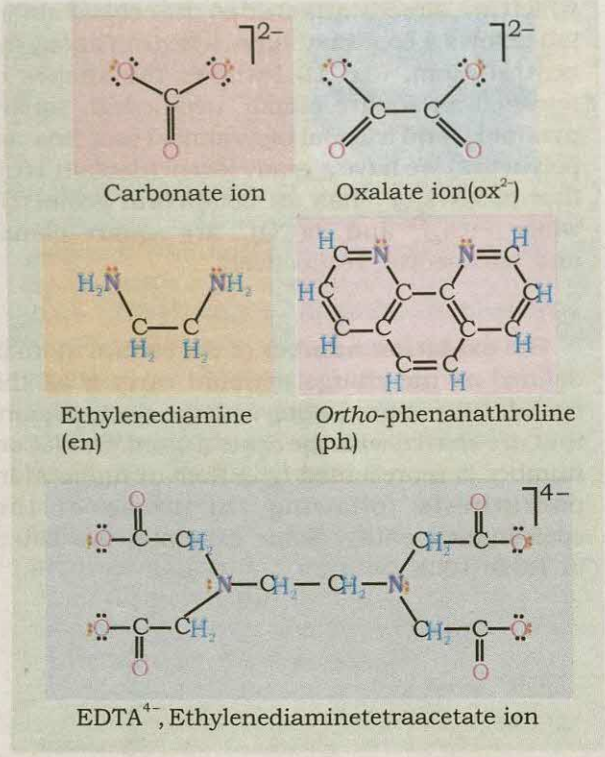


Fig. 10.2 *Structures of some common chelating ligands.*

Didentate chelation

In $[PtCl_2(en)]$, 'en' represents the didentate ligand $NH_2CH_2CH_2NH_2$, i.e., (1,2–ethanediamine or ethylenediamine) [Fig. 10.3(a)].

Tridentate chelation

In the coordination entity $[PtCl(dien)]^+$, the dien, i.e., [N-(2–aminoethyl)–1,2–ethanediamine] is a tridentate ligand [Fig. 10.3 (b)].

Tetradentate chelation

In $[Pt(trien)]^{2+}$, the trien, i.e., [N, N'–bis (2-aminoethyl) – 1, 2 – ethanediamine] represents a tetradentate ligand [Fig. 10.3(c)].

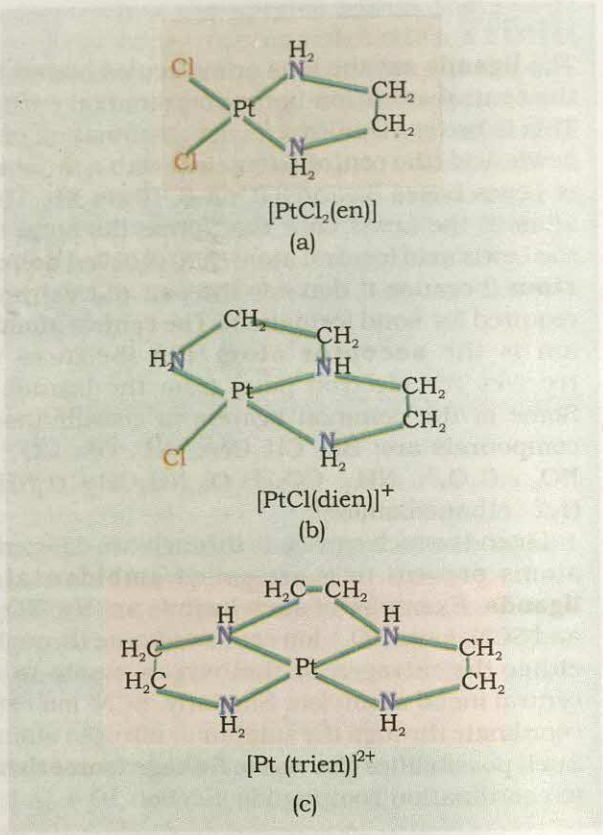


Fig. 10.3 *Examples showing chelaion by: a) en - a didentate, b) dien - a tridentate and c) trien - a tetradentate ligand.*

10.3 NOMENCLATURE OF COORDINATION COMPOUNDS

The coordination entities are formulated and named in accordance with an **additive principle**. For example, while writing the formula, the ligands are added after the central metal atom/ion, as in, $[Co(NH_3)_6]^{3+}$ and in order to name it, the ligand names are added before the name of the central metal/ion. Thus, $[Co(NH_3)_6]^{3+}$ is named as: Hexaamminecobalt(III).

The general rules for writing the formulae and names of mononuclear coordination compounds are as given below.

10.3.1 Rules for writing the Formulae of Mononuclear[2] Coordination Compounds

Mononuclear coordination entities contain a single central metal atom. The sequence of symbols within the formula of a coordination entity is governed by the following rules:

[2] *You will learn about di- and polynuclear coordination entities in your higher studies.*

(i) the central atom is listed first;
(ii) the anionic ligands appear next, listed in an alphabetical order according to the first symbol of their formulae;
(iii) the neutral ligands follow next in an alphabetical order;
(iv) the formula of the coordination entity is enclosed in square brackets. If the ligands are polyatomic, their formulae are enclosed in parantheses;
(v) no space is kept between representations of ionic species within the formula;
(vi) when the formula of a charged coordination entity is written without the formula of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example

$[Co(CN)_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$ etc.

The following examples illustrate the above rules:

$[Co(NH_3)_6]Cl_3$; $[CoCl(NH_3)_5]Cl_2$; $K_2[PtCl_4]$; $[CoCl(NO_2)(NH_3)_4]Cl$; $K_3[Fe(CN)_6]$

10.3.2 Rules for naming of Mononuclear Coordination Compounds

While naming a coordination compound, the rules followed are:

(i) The cation is named first as is the case with other ionic compounds. This rule applies to both positively and negatively charged coordination entities. Thus, in $K_4[Fe(CN)_6]$ and $[Co(NH_3)_6]Cl_3$, K^+ and $[Co(NH_3)_6]^{3+}$ cations are named first.
(ii) Within the coordination entity, the ligands are named in an alphabetical order (without any consideration of charge) before the name of the central atom/ion. For example, $[PtBrCl(NO_2)(NH_3)]^-$ is named as amminebromochloronitrito-N- platinate (II).
(iii) For indicating the number of each kind of ligand within the coordination entity, two kinds of numerical prefixes are used. The simple di-, tri-, tetra-, etc., is used when ligand name is simple. For ligands containing any of these prefixes in their names, their numbers are indicated by prefixes, bis-, tris-, tetrakis-, etc., for example: $[CoCl(NO_2)(NH_3)_4]Cl$ is named as tetraamminechloronitrito-N-cobalt(III) chloride while $[PtCl_2(NH_2CH_2CH_2NH_2)_2](NO_3)_2$ is named as dichlorobis (1,2 - ethanediamine) platinum(IV) nitrate.
(iv) The names of anionic ligands, organic or inorganic, end in -o. In general, if the anionic ligand name ends in -ide, -ite, or -ate, the final 'e' is replaced by 'o' , giving -ido, -ito and –ato, respectively. For example, chloro, nitrito, carbonato, oxalato, etc. For inorganic anionic ligands containing numerical prefixes, such as triphosphate, enclosing marks ( ) are added, i.e., (triphosphate). Neutral and cationic ligand names are used as such, except, aqua (for water), ammine (for ammonia), carbonyl (for carbon monoxide) and nitrosyl (for NO). These are placed within enclosing marks.
(v) The oxidation number of the central atom is indicated in Roman numerals after its name placed in enclosing marks. No space is left between this number and the rest of the name.

Example 10.2
Write the formulae for the following coordination compounds:
(i) tetrahydroxozincate(II)
(ii) Pentaaquachlorochromium(III) chloride
(iii) tetrabromocuprate(II)
(iv) pentacarbonyliron(0)
(v) potassium tetracyanocuprate(II)

Solution
(i) $[Zn(OH)_4]^{2-}$ (ii) $[CrCl(H_2O)_5]Cl_2$ (iii) $[CuBr_4]^{2-}$ (iv) $[Fe(CO)_5]$ (v) $K_2[Cu(CN)_4]$

Example 10.3
Write the systematic names of the following coordination entities and compounds:
(i) $[CoCl_2(NH_3)_4]^+$ (ii) $[CrCl_3(NH_3)_3]$
(iii) $K_3[Cr(C_2O_4)_3]$ (iv) $K_4[Fe(CN)_6]$
(v) $[PtCl(NH_3)_5]Cl_3$

Solution
(i) tetraamminedichlorocobalt(III)
(ii) triamminetrichlorochromium(III)
(iii) potassium trioxalatochromate(III)
(iv) potassium hexacyanoferrate(II)
(v) pentaamminechloroplatinum(IV) chloride.

10.4 ISOMERISM IN COORDINATION COMPOUNDS

Isomers are compounds having same molecular formula but different structures. Coordination compounds show the following types of isomerism.

Examples illustrating the use of rules of nomenclature for coordination compounds

Formula of Coordination Compound	Name of Coordination Compound
$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate(III)
$[CoCl(NH_3)_5]Cl_2$	Pentaamminechlorocobalt(III) chloride
$[PtCl(NH_2CH_3)(NH_3)_2]Cl$	Diamminechloro(methylamine)platinum(II) chloride
$K_2[PdCl_4]$	Potassium tetrachloropalladate(II)
$Na[PtBrCl(NO_2)(NH_3)]$	Sodium amminebromochloronitrito-N-platinate(II)
$[Co(H_2O)_2(NH_3)_4]Cl_3$	Tetraamminediaquacobalt(III) chloride
$[PtCl_2(C_5H_5N)(NH_3)]$	Amminedichloro(pyridine)platinum(II)
$[Ni(H_2O)_2(NH_3)_4]SO_4$	Tetraamminediaquanickel(II) sulphate
$K_2[Ni(CN)_4]$	Potassium tetracyanonickelate(II)
$[Co(NH_3)_6]Cl(SO_4)$	Hexaamminecobalt(III) chloride sulphate
$Fe_4[Fe(CN)_6]_3$	Iron(III) hexacyanoferrate(II)

10.4.1 Geometric Isomerism

This type of isomerism is of importance in square-planar, $[Ma_2b_2]$ and octahedral, $[Ma_2b_4]$, coordination entities like $[PtCl_2(NH_3)_2]$ and $[CoCl_2(NH_3)_4]^+$, respectively. If the same ligands (more specifically the donor atoms) occupy adjacent positions in the coordination polyhedron, we have the cis-isomer, and if the positions occupied are opposite to each other, the trans-isomer results (Figs. 10.4 and 10.5).

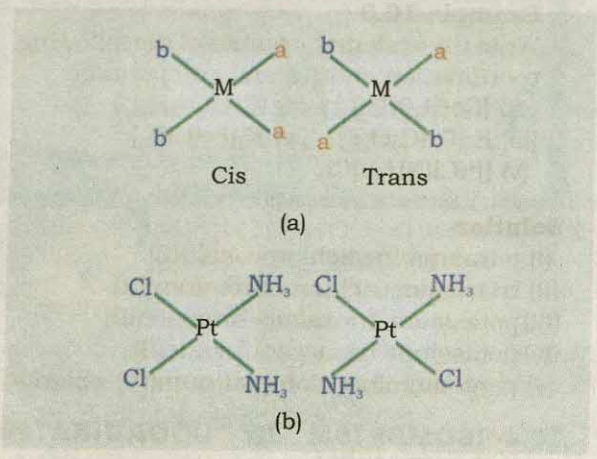


Fig. 10.4 *(a) Representation of geometric isomers of the square-planar, $[Ma_2b_2]$ type of coordination entities; and*
(b) the geometric isomers (cis and trans) of $[PtCl_2(NH_3)_2]$.

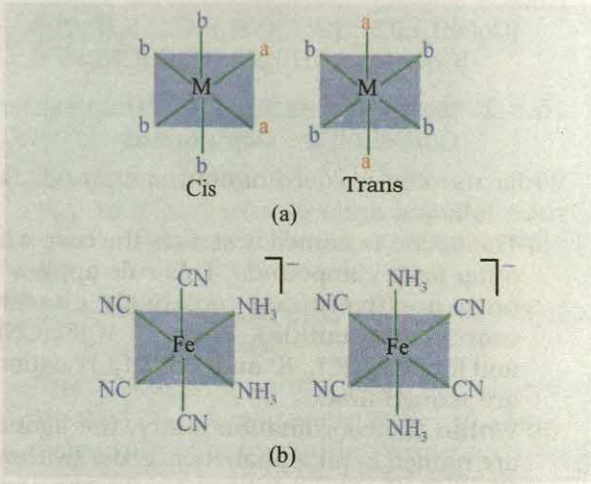


Fig. 10.5 *(a) Representation of the geometric isomers of octahedral, $[Ma_2b_4]$ type of coordination entities; and*
(b) the geometric (cis and trans) isomers of $[Fe(CN)_4(NH_3)_2]^-$.

Another type of geometrical isomerism occurs in octahedral coordination entities of the type $[Ma_3b_3]$ like $[Co(NO_2)_3(NH_3)_3]$. If each trio of donor atoms occupy adjacent positions at the corners of an octahedral face, we have the **facial (fac) isomer**. When the positions are around the meridian of the octahedron,we get the **meridional (mer) isomer** (Fig. 10.6). Geometric isomers differ in their physical characteristics, out of which, dipole moments and visible/UV spectra are important.

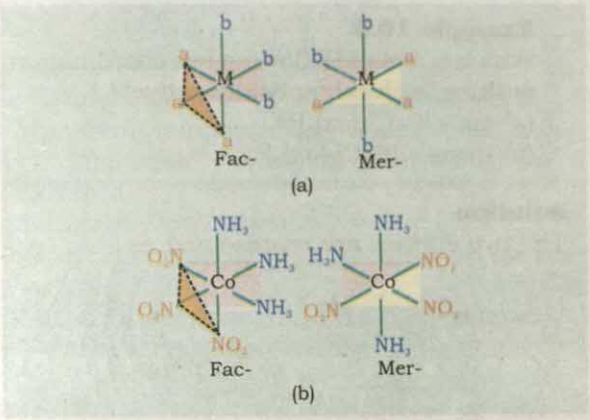


Fig. 10.6 *(a) The facial (fac) and meridional (mer) geometric isomers of the octahedral $[Ma_3b_3]$ type of coordination entities; and (b) the fac- and mer- isomers of $[Co(NO_2)_3(NH_3)_3]$.*

10.4.2 Optical Isomerism

Optical isomers (also called enantiomorphs or enantiomers), are pairs of molecules (with same molecular formula) which are non-superimposable mirror images of each other. Optical isomers possess the property of **chirality** (handedness). The optical isomers of a compound have identical physical and chemical properties. The only distinguishing property is that the isomers rotate the plane of polarised light either to left or to the right. When the rotation is to the left, the isomer is called **laevorotatory** (*l* or –), and when the rotation is to the right, the isomer is designated as **dextrorotatory** (*d* or +). A 1:1 equilibrium mixture of the d and *l* isomers gives a **racemic mixture** with a net zero rotation. Numerous examples of optical isomerism are provided by octahedral coordination compounds having chelating ligands. Some of the examples are:

(i) The enantiomers of $[Cr(C_2O_4)_3]^{3-}$ are shown in Fig. 10.7.

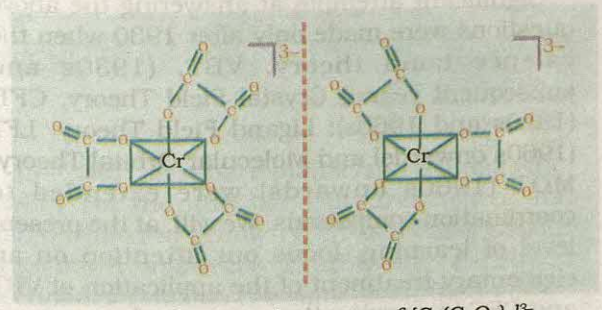


Fig. 10.7 *Optical isomers of $[Cr(C_2O_4)_3]^{3-}$.*

(ii) In a coordination entity of the type $[PtCl_2(en)_2]^{2+}$, only the cis-isomer shows optical activity. The two unidentate ligands (in this case the Cl^- ions) have to be cis-cis to each other (Fig. 10.8).

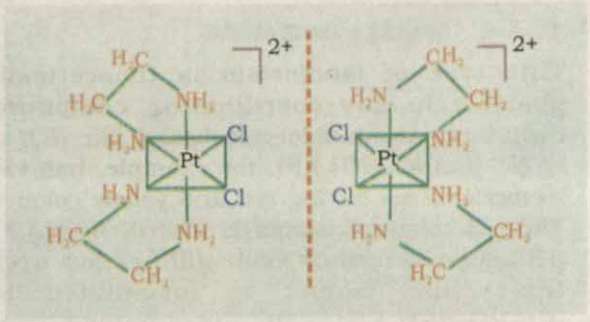


Fig. 10.8 *Optical isomers of cis-$[PtCl_2(en)_2]^{2+}$.*

(iii) In the case of coordination entity, $[CrCl_2(NH_3)_2(en)]^+$, the geometrical isomer having cis-cis configuration with respect to the unidentate ligands (in this case, the chloride ions and the ammonia groups) can only be resolved into the *d*- and *l* - isomers, (Fig. 10.9).

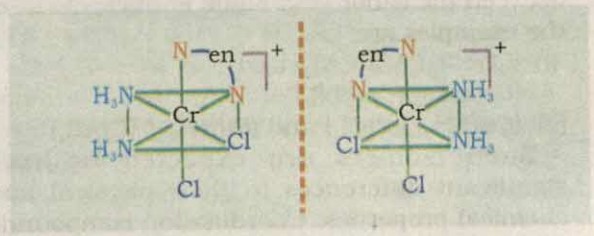


Fig. 10.9 *Optical isomers of $[CrCl_2(NH_3)_2(en)]^+$. Here en represents $H_2NCH_2CH_2NH_2$.*

10.4.3 Ionisation Isomerism

This type of isomerism occurs when the counter ion in a coordination compound is itself a potential ligand. Thus, the pairs of the following compounds:

(i) $[Co(NO_3)(NH_3)_5]SO_4$, and $[Co(SO_4)(NH_3)_5]NO_3$

(ii) $[PtCl_2(NH_3)_4]Br_2$, and $[PtBr_2(NH_3)_4]Cl_2$ produce different ions in solution.

A special form of ionisation isomerism is the so called **Hydrate isomerism**. It occurs when water forms a part of the coordination entity or is outside it. For example, $CrCl_3.6H_2O$ exists in three distinct isomeric forms:

$[Cr(H_2O)_6]Cl_3$, violet; $[CrCl(H_2O)_5]Cl_2.H_2O$, pale

green; $[CrCl_2(H_2O)_4]Cl\ 2H_2O$, dark green. Apart from their distinctive colours, the three isomers can be identified by the addition of excess of aqueous silver nitrate to their aqueous solutions, which precipitates chloride in the molar ratio of 3:2:1 respectively.

10.4.4 Linkage Isomerism

This type of isomerism is theoretically possible in any coordination compound containing an ambidentate ligand like NO_2^- or SCN^-. $[Co(NO_2)(NH_3)_5]^{2+}$, for example, has two isomeric forms having red and yellow colours. The red coloured isomer is $[Co(ONO)(NH_3)_5]^{2+}$, pentaamminenitrito-O-cobalt(III) cation while the yellow isomer is formulated as $[Co(NO_2)(NH_3)_5]^{2+}$. It is named as: pentaamminenitrito-N-cobalt(III) cation. In the first cation we have Co-(ONO) link, while in the second case, NO_2^- coordinates to the metal ion through the nitrogen atom, Co-(NO_2).

10.4.5 Coordination Isomerism

Coordination compounds made up of cationic and anionic coordination entities show this type of isomerism due to the interchange of ligands between the cation and anion entities. Some of the examples are:

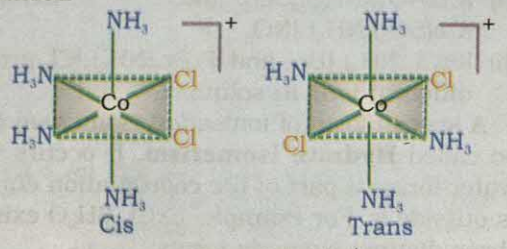
(i) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

(ii) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4]\ [CuCl_4]$

Such isomers are expected to have significant differences in their physical and chemical properties. Coordination compounds also exhibit polymerisation and ligand isomerism. You will learn about these in your higher studies.

Example 10.4
Draw structures of geometrical isomers of $[CoCl_2(NH_3)_4]^+$.

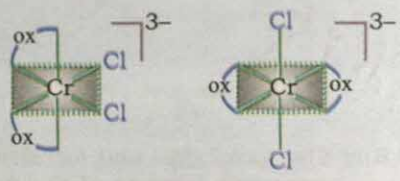
Solution



$[CoCl_2(NH_3)_4]^+$

Example 10.5
Which out of the following two coordination entities is chiral (optically active)?
(a) cis - $[CrCl_2(ox)_2]^{3-}$
(b) trans - $[CrCl_2(ox)_2]^{3-}$.

Solution
The two entities are represented as



(a) Cis-$[CrCl_2(ox)_2]^{3-}$ (B) trans-$[CrCl_2(ox)_2]^{3-}$

Out of the two, (a) cis-$[CrCl_2(ox)_2]^{3-}$ is chiral (optically active).

10.5 BONDING IN COORDINATION COMPOUNDS

The nature of bonding, in coordination compounds, as presented in Werner's theory, is not based on any sound theoretical principles. After the recognition of the importance of electron in the formation of chemical bonds, Sidgwick and Lowry suggested that the primary and secondary linkages of Werner's theory were, in fact, ionic and covalent (coordinate) bonds respectively.

The Werner theory cannot answer basic questions like:

(i) Why only certain elements possess the remarkable property of forming coordination compounds?

(ii) Why the bonds in coordination compounds have directional properties?

(iii) Why coordination compounds have characteristic magnetic and optical properties?

Significant attempts at answering the above questions were made only after 1930 when the valence bond theory, VBT, (1930s and subsequent years); Crystal Field Theory, CFT, (1950s and 1960s); Ligand Field Theory, LFT (1960s onwards) and Molecular Orbital Theory, MOT (1960s onwards) were extended to coordination compounds. We will, at the present level of learning, focus our attention on an elementary treatment of the application of VBT and CFT to coordination compounds.

10.5.1 Valence Bond treatment of Coordination Compounds

The valence bond theory, VBT, was extended to coordination compounds by Linus Pauling in 1931. The basic principles involved in this treatment are:

(i) Orbital hybridization,
(ii) Bonding between ligand and the metal ion/atom, and
(iii) Relation between the observed magnetic behaviour and the bond type.

The basic premise of hybridization is that appropriate linear combinations of non-equivalent orbitals of an atom give sets of hybrid orbitals that are equivalent and have specific spatial orientations. We learnt about *sp*, sp^2 and sp^3 hybridisation schemes in Class XI. For coordination compounds, the hybridizations involving *s*, *p* and *d* orbitals are important. Different linear combinations of *s*, *p* and *d* orbitals, like dsp^2, dsp^3 and d^2sp^3 yield **square planar**, **trigonal-bipyramidal** or **square-pyramidal** and **octahedral** spatial arrangements commonly encountered in coordination compounds (Fig. 10.1).

Pd(II), Pt(II) and Ni(II) form mostly the 4-coordinate, square-planar, diamagnetic coordination entities. In their ground states, the free ions, Pd^{2+}, Pt^{2+} and Ni^{2+} (all d^8 ions), are paramagnetic. **Square-planar hybridization requires one d, one s and two p orbitals for the formation of dsp^2 hybrids. It is these hybrid orbitals which participate in sigma bond formation with ligands**. For one *d* orbital to be available for hybridisation, pairing of electrons takes place in the remaining *d* orbitals, as shown below in the case of $[Ni(CN)_4]^{2-}$.

	3d					*4s*	*4p*		
Ni	↑↓	↑↓	↑↓	↑	↑	↑↓			
Ni^{2+}	↑↓	↑↓	↑↓	↑	↑				
$[Ni(CN)_4]^{2-}$	↑↓	↑↓	↑↓	↑↓		↑↓ CN^-	↑↓ CN^-	↑↓ CN^-	↑↓ CN^-

dsp^2 hybrids used

$[Ni(CN)_4]^{2-}$ is square planar and diamagnetic. $[NiCl_4]^{2-}$, on the other hand, is paramagnetic and has tetrahedral geometry. In this case, the VB treatment assumes that i) the *d*-orbital occupancy remains the same as in the free Ni^{2+} ion and ii) the metal uses sp^3 hybrids (involving *4s* and *4p* orbitals) for bonding with the ligands as shown below:

$[NiCl_4]^{2-}$ is paramagnetic as there are two unpaired electrons.

	3d					*4s*	*4p*		
Ni	↑↓	↑↓	↑↓	↑	↑	↑↓			
Ni^{2+}	↑↓	↑↓	↑↓	↑	↑				
$[NiCl_4]^{2-}$	↑↓	↑↓	↑↓	↑	↑	↑↓ Cl^-	↑↓ Cl^-	↑↓ Cl^-	↑↓ Cl^-

sp^3 hybrids used

The two coordination entities $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$ illustrate the useful generalisation called, **the magnetic criteria of the bond type. That is, the geometry of the coordination entity can be predicted if its magnetic behaviour is known**. In the above cases, we find that diamagnetic species is square-planar while the paramagnetic is tetrahedral.

The VB theory explains the formation of 6 coordinate, octahedral coordination entities by invoking the use of $(n\text{-}1)d^2nsnp^3$ or $nsnp^3nd^2$ hybrid orbitals by the central metal ion in forming bonds with the ligands. An example involving use of $(n\text{-}1)d^2nsnp^3$ hybrids is the coordination entity, $[Fe(CN)_6]^{4-}$.

The double occupancy of $(n\text{-}1)d$ orbitals confers extra stability and the absence of unpaired electrons renders this entity diamagnetic.

	$(n\text{-}1)d$					*ns*	*np*		
Fe	↑↓	↑	↑	↑	↑	↑↓			
Fe^{2+}	↑↓	↑	↑	↑	↑				
$[Fe(CN)_6]^{4-}$	↑↓	↑↓	↑↓	↑↓ L	↑↓ L	↑↓ L	↑↓ L	↑↓ L	↑↓ L

(d^2sp^3 hybrid orbitals filled by electron pairs donated by the respective ligands. L = CN^-).

Co^{3+} is isoelectronic with Fe^{2+} and forms the diamagnetic entity $[Co(NH_3)_6]^{3+}$.

Example 10.6
Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.

Solution
Pt^{2+} is a d^8 ion. For square-planar geometry, dsp^2 hybrids are required. For the availability of one d orbital, pairing of electrons takes place in the remaining *d* orbitals. Hence there are no unpaired electrons in $[Pt(CN)_4]^{2-}$ ion.

While the VB theory, to a large extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following shortcomings:

- A number of assumptions are involved
- There is no quantitative interpretation of magnetic data
- It has nothing to say about the spectral properties of coordination compounds
- It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds
- It does not make exact predictions regarding the tetrahedral and square-planar structures of 4-coordinate complexes
- It does not distinguish between strong and weak ligands.

The drawbacks of VBT of coordination compounds are, to a considerable extent, removed by the **Crystal Field Theory,** which we take up next for discussion.

10.5.2 Crystal Field Theory

The Crystal Field Theory (CFT) was originally proposed for explaining the optical properties of crystalline solids. It was applied to the study of coordination compounds in the 1950s. CFT assumes the ligands to be point charges and the interaction between them and the electrons of the central metal to be electrostatic in nature. The five *d* orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the *d* orbitals is lifted. It results in splitting of the *d* orbital energies. The pattern of splitting depends upon the nature of the crystal field. **The splitting of *d* orbital energies and its effects, in fact, form the basis of the crystal field treatment of coordination compounds.** We will first consider:

(A) Crystal Field Effects in Octahedral Coordination Entities.

For convenience, let us assume that the six ligands are positioned symmetrically along the cartesian axes, with the metal atom at the origin. As the ligands approach, first there is an increase in the energy of *d* orbitals relative to that of the free ion just as would be the case in a spherical field. Next, the orbitals lying along the axes (d_{z^2} and $d_{x^2-y^2}$) get repelled more strongly than d_{xy}, d_{yz} and d_{xz} orbitals, which have lobes directed between the axes. The d_{z^2} and $d_{x^2-y^2}$ orbitals get raised in energy and d_{xy}, d_{yz}, d_{xz} orbitals are lowered in energy relative to the average energy in the spherical crystal field. Thus, the degenerate set of *d* orbitals get split into two sets: the lower energy orbital set, t_{2g} and the higher energy, e_g set. The energy separation is denoted by Δ_o (the subscript o is for octahedral) (Fig. 10.10).

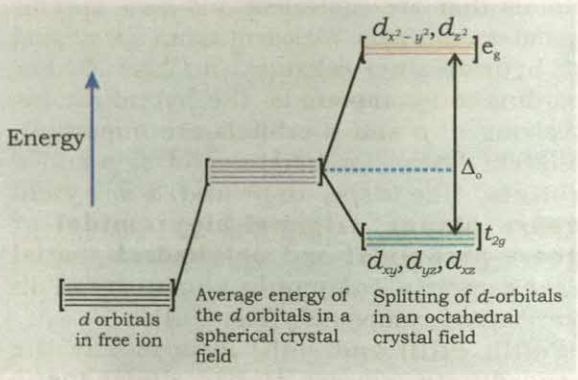


Fig. 10.10 *d orbital splitting in an octahedral crystal field.*

Let us now learn about the significance of Δ_o by considering first the d^1 coordination entity, $[Ti(H_2O)_6]^{3+}$, formed in aqueous solutions of $Ti^{3+}(d^1)$ ion. Obviously, the single *d* electron occupies one of the lower energy t_{2g} orbitals. In d^2 and d^3 coordination entities, the d electrons occupy the t_{2g} orbitals singly in accordance with the Hund's rule. For d^4 ions, two possible patterns of electron distribution arise: i) the fourth electron may enter an e_g orbital (of higher energy) or ii) it may pair an electron in the t_{2g} level. **The actual configuration adopted is decided by the relative values of Δ_o and P. P represents the energy required for electron pairing in a single orbital.**

If Δ_o is less than P ($\Delta_o < P$), we have the so called **weak field, high spin situation**, and the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3\ e_g^1$. If now a fifth electron is added to a weak field coordination entity, the configuration becomes $t_{2g}^3\ e_g^2$.

When $\Delta_o > P$, we have the **strong field, low spin situation,** and pairing will occur in the t_{2g} level with the e_g level remaining unoccupied in entities of d^1 to d^6 ions. **Calculations show that coordination entities with four to seven *d* electrons are more stable for strong field as compared to weak field cases.**

(B) Crystal Field Effects in Tetrahedral Coordination Entities

In tetrahedral coordination entity formation, the d orbital splitting (Fig. 10.11) is inverted and smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t \simeq -(4/9)\Delta_o$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

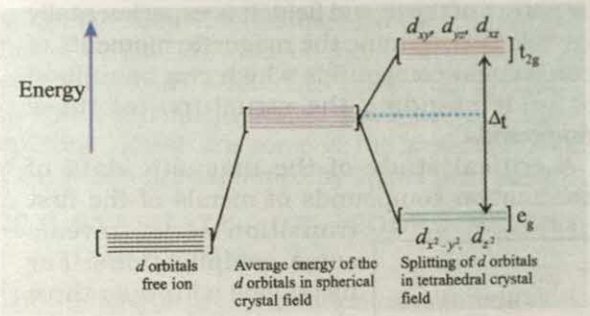


Fig. 10.11 *d orbital splitting in a tetrahedral crystal field.*

Important factors which determine the magnitude of Δ the orbital splitting energy, are:

(i) Oxidation state of the metal ion: Generally, the higher the ionic charge on the central metal ion, the greater the value of Δ.

(ii) Nature of the metal ion: For analogous entities within a group, the Δ values differ. The general trend being *3d <4d<5d*. Thus while going from Cr to Mo or Co to Rh, the Δ_o value increases by ~50%. As a consequence of this, coordination entities of the second and third transition series have a greater tendency to be low spin as compared to the first transition series.

(iii) Geometry of the coordination entity: The Δ_t value is only ~50% as large as that of Δ_o.

(iv) Nature of the ligand: The ligands can be arranged in the order of increasing field strength.

10.5.3 Colour in Coordination Compounds

Coordination compounds of transition metals have fascinating colours. Colours of transition metal ions in aqueous solution correspond to the presence of their aqua complexes. Further, while aqueous solution of octahedral $[Co(H_2O)_6]^{2+}$ is pink, that of tetrahedral $[CoCl_4]^{2-}$ is blue. The colour of aqueous $[Ni(H_2O)_6]^{2+}$ turns blue when ammonia is added to it, giving $[Ni(NH_3)_6]^{3+}$. Violet $[Cr(H_2O)_6]^{3+}$ gives bright blue $[Cr(H_2O)_6]^{2+}$ upon reduction. We know that the colour of a substance is due to the absorption of light at a specific wavelength in the visible part of the electromagnetic spectrum (400 to 700nm) and transmission or reflection of the rest of the wavelengths. An object that absorbs all visible light appears black. Table 10.3 gives the relationship of the wavelength absorbed and the colour observed. The mechanism of light absorption in coordination compounds is that photons of appropriate energy can excite the coordination entity from its ground state to an excited state. The details of the exact mechanism are beyond the scope of this book. However, in the case of copper(II) ions in solution, for example, it can be imagined that one of the *d*-electrons from the t_{2g} set (d_{xy}, d_{yz}, d_{xz}) gets excited to the e_g set ($d_{x^2-y^2}$, d_{z^2} orbitals). In this case since high energy is transmitted it means that low energy light (red region) is absorbed. For copper(II) ions in aqueous solution, the energy gap Δ_o is relatively small.

By using spectroscopic data for a number of coordination compounds having the same metal ion but different ligands, the crystal field splitting for each ligand has been calculated and the **spectrochemical series:**

Change in colour by changing ligand species. Left, an aqueous cobalt (II) chloride solution. The pink colour is due to the $[Co(H_2O)_6]^{2+}$ ions. Right, after the addition of HCl solution, pink colour turns blue because of the formation of complex $[CoCl_4]^{2-}$.

Table 10.3 Relationship between the wavelength of light absorbed and the colour observed in some coordination entities

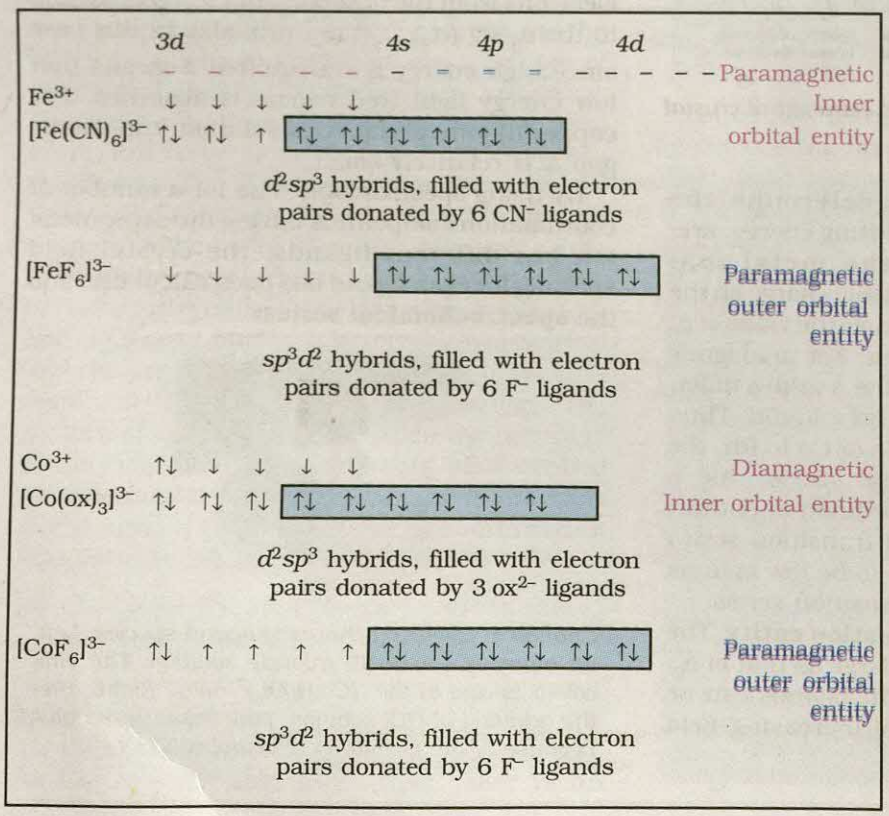
Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow Orange
$[Co(CN)_6]^{3-}$	310	Ultraviolet	Pale Yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$[Ti(H_2O)_6]^{3+}$	498	Blue Green	Purple

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < py, NH_3 < CN^- < CO$ established which helps in understanding the nature of bonding and structures of these compounds.

10.5.4 Magnetic Properties of Coordination Compounds

Additional information for understanding the nature of coordination entities is provided by **magnetic susceptibility measurements**. We have noted that coordination compounds generally have partially filled *d* orbitals and as such they are expected to show characteristic magnetic properties depending upon the oxidation state, electron configuration, coordination number of the central metal and the nature of the ligand field. It is experimentally possible to determine the magnetic moments of coordination compounds which can be utilized for understanding the structures of these compounds.

A critical study of the magnetic data of coordination compounds of metals of the first transition series reveals some complications. For metal ions with upto three electrons in the *d* orbitals, like $Ti^{4+}(d^0)$; $Ti^{3+}(d^1)$; $Ti^{2+}(d^2)$; V^{2+} and Cr^{3+} (d^3); two vacant *d* orbitals are available for octahedral hybridization with *4s* and *4p* orbitals. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three *3d* electrons are present, the required pair of *3d* orbitals for octahedral hybridization is not directly available (as a consequence of Hund's rule). Thus, for d^4 (Cr^{2+}, Mn^{3+}), $d^5(Mn^{2+}, Fe^{3+})$, $d^6(Fe^{2+}, Co^{3+})$ cases, a vacant pair of d-orbitals results only by pairing of *3d* electrons which leaves respectively two, one and zero electrons, unpaired.



The magnetic data agree with maximum spin pairing in many cases, especially with coordination compounds containing d^6 ions. However, with species containing d^4 and d^5 ions there are complications. $[Fe(CN)_6]^{3-}$ has magnetic moment of a single unpaired electron while $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons. $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)_3]^{3-}$ is diamagnetic. This apparent anomaly is explained by VB theory in terms of formation of **inner orbital** and **outer orbital** coordination entities (See box on page 210).

The crystal field model is successful in explaining the formation, structures, optical and magnetic properties of coordination compounds to a large extent. However, from the assumption that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. The anionic ligands actually are found at the low end of the spectrochemical series. Also OH^- which lies below H_2O and NH_3 in spectrochemical series, produces a greater splitting. These are some of the weaknesses of CFT, which are explained by ligand field theory.

10.6 STABILITY OF COORDINATION COMPOUNDS

The stability of a coordination compound $[ML_n]$ is measured in terms of the stability constant (equilibrium constant), given by the expression,

$$\beta_n = [ML_n]/[M(H_2O)_n]\,[L]^n$$

for the overall reaction:

$$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$$

By convention, the water displaced is ignored, as its concentration remains essentially constant. The above overall reaction takes place in steps, with a stability (formation) constant, K_1, K_2, K_3,....., K_n for each step as represented below:

$$M(H_2O)_n + L \rightleftharpoons ML(H_2O)_{n-1} + H_2O$$
$$K_1 = [ML(H_2O)_{n-1}]\,/\{[M(H_2O)_n]\,[L]\}$$
$$ML_{n-1}(H_2O) + L \rightleftharpoons ML_n + H_2O$$
$$K_n = [ML_n]\,/\{[ML_{n-1}(H_2O)]\,[L]\}$$

$$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$$
$$\beta_n = K_1 \times K_2 \times K_3 \times ..... \times K_n$$

β_n, the stability constant, is related to thermodynamic stability when the system has reached equilibrium. Most of the measurements have been made from aqueous solutions, which implies that the complex is formed by the ligand displacing water from the aqua complex of the metal ion. Ignoring the charge and taking L as an unidentate ligand, the stepwise formation of the complex is represented as shown above. K_1, K_2, K_3 ..... K_n representing the stepwise stability (or formation) constants.

Important generalizations derived from the vast data on stability constants are:

- For a given metal and ligand the stability is generally greater, the greater the charge on the metal ion. Thus, stability of coordination entities of ions of charge 3+ is greater than the entities of 2+ ions. Further, for the divalent ions of the first row transition elements, irrespective of the ligand involved, the stabilities vary in the **Irving-Williams Order**: $Mn^{II} < Fe^{II} < Co^{II} < Ni^{II} < Cu^{II} > Zn^{II}$.
- The metal ions, **'class a' acceptors** like metals of groups 1 and 2, the inner transition elements and the early members of the transition series (groups 3 to 6) form their most stable coordination entities with ligands containing N, O or F donor atoms.
- The metal ions, **'class b' acceptors** like the transition elements – Rh, Pd, Ag, Ir, Au and Hg having relatively full *d* orbitals form their most stable complexes with ligands whose donor atoms are the heavier members of the N, O and F groups.
- The stability also depends on the formation of chelate rings. If L is an unidentate ligand and L-L, a didentate ligand and if the donor atoms of L and L-L are the same element, then L-L will replace L. The stabilisation due to chelation is called the **chelate effect**. It is of great importance in biological systems and analytical chemistry. The chelate effect is maximum for the 5- and 6-membered rings. In general, rings provide greater stability to the complex.
- If a multidentate ligand happens to be cyclic and there are no unfavourable steric effects, a further increase in stability occurs. This is termed the **macrocyclic effect**.

10.7 ORGANOMETALLIC COMPOUNDS

As per definition, **an organometallic compound must contain, at least one metal-carbon bond**. However, the borderlines between organometallic compounds and other compounds are not always well defined. Thus,

$[Ni(CO)_4]$, is taken as an organometallic compound, though CO is not considered to be an organic compound. Further, the suffix 'metallic', often includes metalloids like boron, silicon, arsenic and tellurium; as well as true metals. By convention, metal cyanides, though possessing an M-C bond are not included in organometallics.

Classification

Two broad divisions of organometallics are:
(i) main group organometallics and
(ii) *d*- and *f*-block organometallics.

Historically, the study of organometallics started with the compounds of main group elements. We will, therefore, take up the chemistry of main group organometallics first.

10.7.1 Main Group Organometallics

E.C. Frankland was the first chemist to synthesise an organometallic compound, dimethylzinc, $(CH_3)_2Zn$, in 1848. In the following 14 years he prepared, $Zn(C_2H_5)_2$, $Hg(CH_3)_2$, $Sn(CH_3)_4$ and $B(CH_3)_3$. He also introduced the term 'organometallic' in the language of chemistry. **Organometallic** compounds of Li, Mg, B, Al and Si received recognition in early years of twentieth century as compounds of industrial importance.

The *s*- and *p*-block organometallics are named according to the substituent names used in organic chemistry. For example, methylithium for CH_3Li and trimethylboron for $B(CH_3)_3$ which is also called trimethylborane, taking it to be a derivative of its hydrogen counterpart. Thus, $Si(CH_3)_4$ and $As(CH_3)_3$ are tetramethylsilane and trimethylarsane respectively.

The oxidation number of the metallic element in an organometallic compound is based on the organic moiety being considered to be anionic. For example, in $Zn(CH_3)_2$, CH_3 group is taken to be negatively charged (1–). Thus, oxidation number of zinc is 2+. The bond in alkyls of *s*-block elements is highly polar ($M^{\delta+}$–$C^{\delta-}$). In the organometallics of groups 14, 15 and 16, the M-C bonds are of relatively low polarity. Methyl compounds of Li, Na, Be, Mg and Al are associated through alkyl bridges and multicentre two-electron bonds. The structures of some representative main group organometallics are shown in Fig. 10.12.

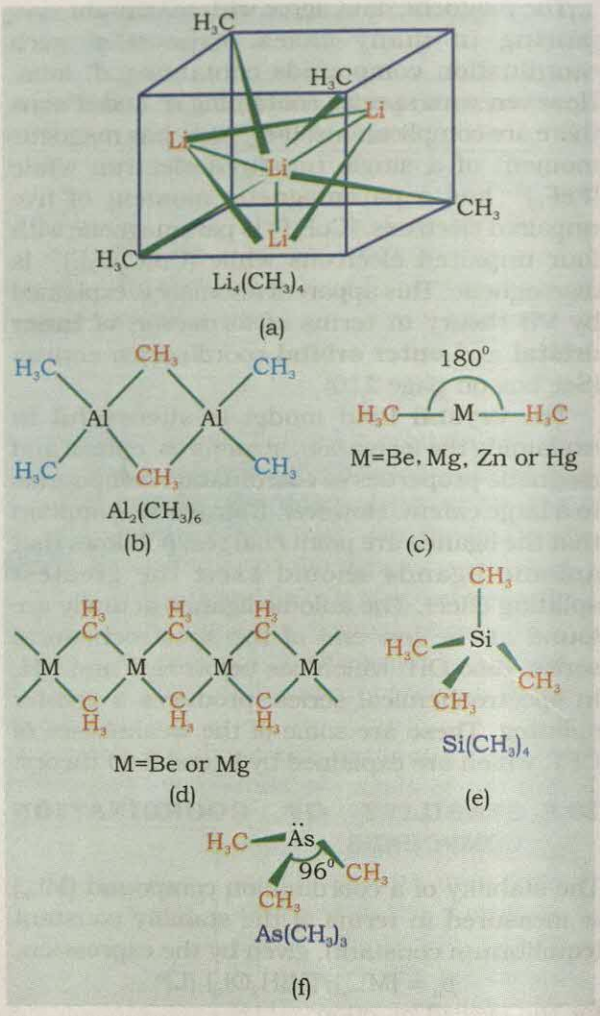


Fig. 10.12 *Structures of some representative main group organometallic compounds.*

Organometallic compounds of electropositive metals are strong reducing agents. They are pyrophoric and ignite spontaneously in air.

10.7.2 *d*- and *f*-block Organometallic Compounds

Historically, the first organometallic compound of a *d*-block element (platinum) was prepared by **W.C. Zeise** in 1827. The compound, trichloroetheneplatinate(II), $[PtCl_3(C_2H_4)]^-$, has the structure shown in Fig. 10.13. Tetracarbonylnickel $[Ni(CO)_4]$, was synthesised by **Mond**, **Langer** and **Quinke** in 1899.

The synthesis of the highly stable bis (cyclopentadienyl)iron(II), **Ferrocene** (Fig. 10.14) in 1951 was a landmark in the advancement of modern organometallic chemistry. **For explaining the stability,**

structure and bonding of ferrocene, the new concept of π–bonding of carbocyclic rings to metal atoms was invoked. This led to the preparation of a large number of organometallic compounds containing benzene and other carbocyclic ligands. Collectively, these compounds are called **metallocenes**. **Ernst Fischer** and **Geoffery Wilkinson** were awarded the **Nobel Prize** in chemistry in 1973 for their prolific contributions in this area of chemistry.

Sir Geoffrey Wilkinson (1921-1996)

Sir Geoffrey Wilkinson, a British chemist had his initial education at Imperial College of Science and Technology, University of London. He worked with Atomic Energy project in Canada, taught at University of California at Berkeley (1946-50), Massachusetts Institute of Technology (1950-51) and Harvard University (1951-55) before returning to Imperial College, London in 1956. He deduced the Structure of *ferrocene*, synthesised many other metallocenes and an important catalyst known as Wilkinson catalyst. For these contributions in organometallic chemistry, he shared Nobel Prize in 1973 with Ernst Otto Fischer, a German chemist.

The so called **sandwich structure** (Fig. 10.14) of ferrocene was confirmed with the help of its IR spectrum and X-ray diffraction analysis. **Walter Kaminsky** and **Hans Brintzinger** showed that metallocenes are highly specific for **homogeneous catalysis processes** like carbonylation, hydrogenation and polymerization.

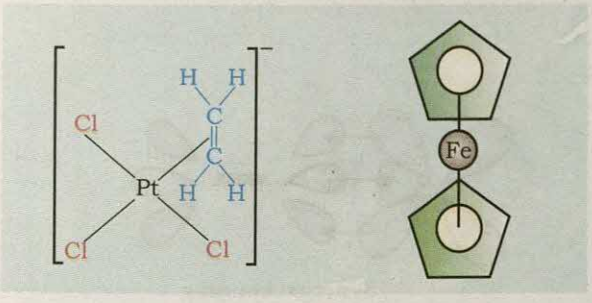


Fig. 10.13 *Structure of* $[PtCl_3(C_2H_4)]^-$.

Fig. 10.14 *Structure of Ferrocene.*

The first *f*-block organometallic compound, $[ThH(OR)(C_5Me_5)_2]$ was prepared in late 1970s. Pentamethylcyclopentadienyl ligand, C_5Me_5, forms stable *f*-block compounds.

10.7.3 Metal Carbonyls

A widely studied and important class of organometallic compounds is that of metal carbonyls. The **homoleptic carbonyls** (compounds containing carbonyl ligands only) are formed by most of the transition metals (*d* metals). The metals constituting the central part of the *d* block form stable, neutral binary carbonyls like: $[V(CO)_6]$, $[Cr(CO)_6]$, $[Mo(CO)_6]$, $[W(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, $[Co_2(CO)_8]$, $[Co_4(CO)_{12}]$, $[Ni(CO_4)]$, etc. Outside the central part of *d*-block, the metal carbonyls are usually unstable.

10.7.4 Metal Carbonyls – Structure and Bonding

Homoleptic binary metal carbonyls have simple, well-defined structures. Tetracarbonylnickel(0) is tetrahedral, pentacarbonyliron(0) is trigonal bipyramidal while hexacarbonylchromium(0) is octahedral. Decacarbonyldimanganese(0) is made up of two square pyramidal $Mn(CO)_5$ units joined by a Mn-Mn bond. Octa-carbonyldicobalt(o) has a Co-Co bond bridged by two CO groups (Fig. 10.15).

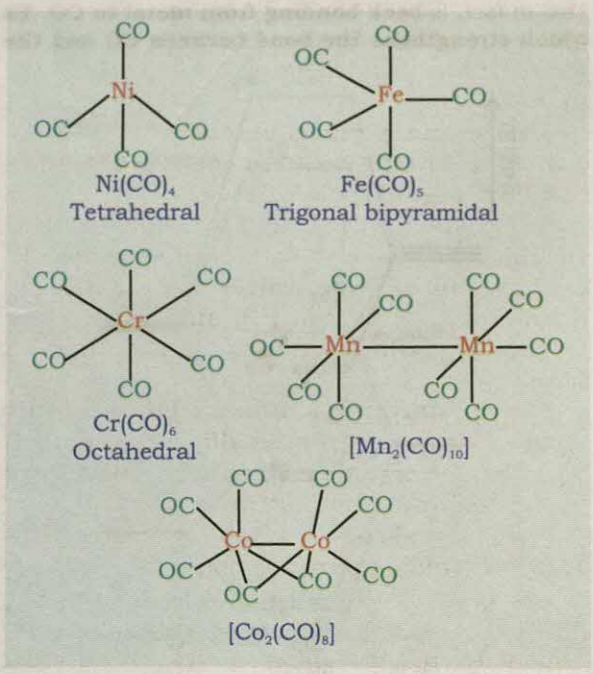


Fig. 10.15 *Structures of some representative homoleptic metal carbonyls.*

Metal carbonyls are mostly solids at room temperature and pressure. Exceptions being iron

and nickel carbonyls which are liquids. The mononuclear carbonyls are volatile and toxic. With the exception of $Fe_2(CO)_9$, nona-carbonyldiiron(0), carbonyls are soluble in hydrocarbon solvents. Mononuclear carbonyls are either colourless or light-coloured. For example, $Fe(CO)_5$ is light straw-coloured liquid. Polynuclear carbonyls are more deeply coloured. $Fe_3(CO)_{12}$, dodecacarbonyltriiron(0), for example, is a deep grass green solid. The reactivity of metal carbonyls is due to (a) the metal centre of the carbonyl, and (b) the CO ligands. Metal carbonyls find use as industrial catalysts and as precursors in organic synthesis.

The bonding in organometallic compounds in general and in carbonyls in particular is best explained by the molecular orbital theory. **Carbon monoxide, CO, as a ligand binds itself to metal atoms through the carbon atom. It is a weak donor. It forms a weak σ bond to the central metal atom. CO is also an acceptor ligand and forms a π bond with the metal. This characteristic property of back bonding stabilises the metal-ligand interaction** (see box given below for a more detailed explanation).

10.8 IMPORTANCE AND APPLICATIONS OF COORDINATION AND ORGANO METALLIC COMPOUNDS

- Studies in the areas of coordination and organometallic chemistry have led to evolution of new bonding concepts and these in turn have produced prolific and entirely new work in this area of study, especially so in organometallics.

For a better understanding of the **nature of bonding in metal carbonyls**, we have to consider first the molecular orbital energy level diagram of carbon monoxide given in fig. 10.16. The highest occupied 3σ molecular orbital in CO is essentially a lobe projecting away from the carbon atom. When CO acts as a ligand, this orbital serves as a weak donor to the metal atom, and forms a bond as represented in Fig 10.17. The lowest unoccupied molecular orbitals of CO are the π* (2π) orbitals. These play an important part in bonding as they can overlap metal *d* orbitals having π symmetry. The resultant interaction leads to the delocalisation of electrons from, filled *d* orbitals on the metal into the empty orbitals on the CO ligands. This in fact, is **back bonding from metal to CO. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal** (Fig. 10.17).

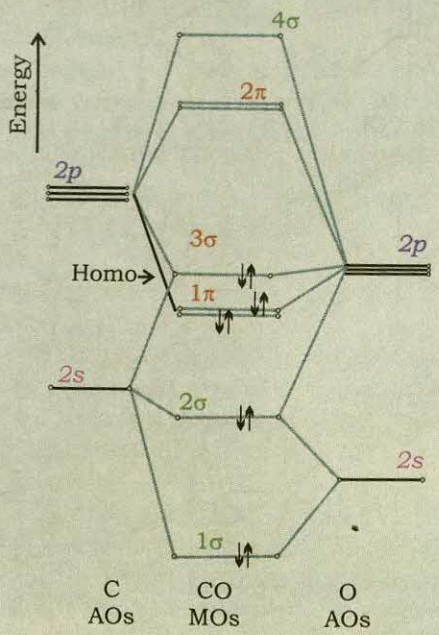
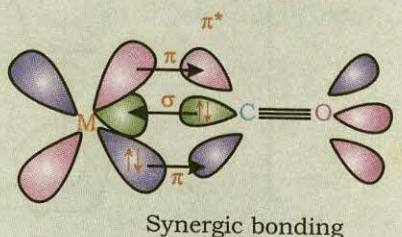


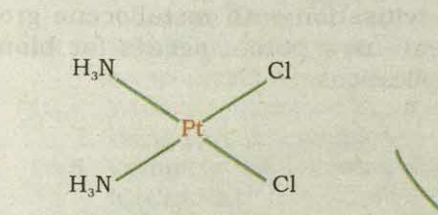
Fig. 10.16 *The MO energy level diagram for CO. The filled 3σ and the vacant 2π orbitals are important for bonding in the formation of metal carbonyls.*



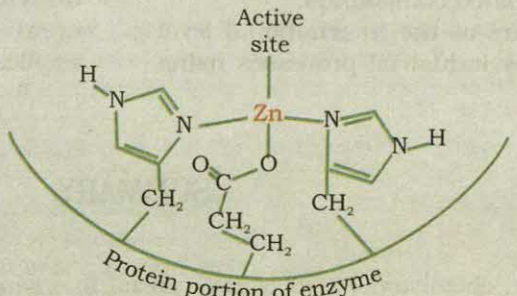
Synergic bonding

Fig. 10.17 *Example of synergic bonding interactions in a carbonyl complex.*

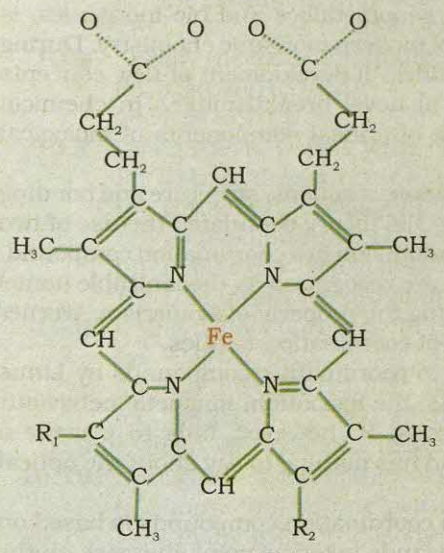
- Coordination compounds are of great importance in biological systems. Familiar examples being – chlorophylls (the green pigments in plants, central to photosynthesis); haemoglobin (the red pigment of blood, which acts as oxygen carrier) alongwith myoglobin (which stores oxygen and is a regulator of respiration); Vit B_{12}, cyanocobalammine, the anti-pernicious anaemia factor. All of these, respectively, are the coordination compounds of magnesium, iron and cobalt with the macrocyclic porphyrin and corrin ligands. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).
- There are many examples of the use of coordination compounds in qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially the chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Most of these reactions are highly specific and sensitive under controlled experimental conditions. Often the detection/estimation limits tend to parts per million (ppm), or even parts per billion (ppb) levels. Familiar examples of such reagents are: ethylenediaminetetraaceticacid (EDTA), dimethylglyoxime, α-nitroso β-naphthol, cupron, etc.
- Some important extraction processes of metals, like those of extraction of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the



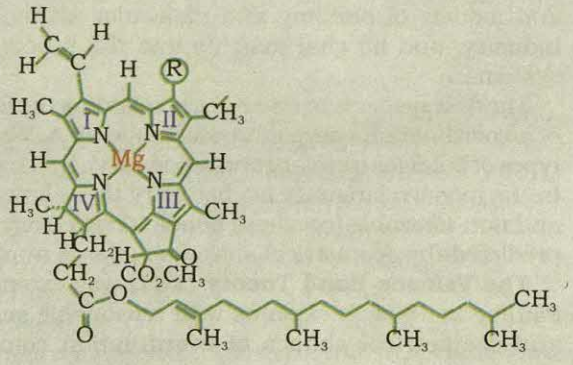
Cis-platin
[Anti-cancer agent]



Carboxypeptidase-A



HEME
Heme B: [R_1 = R_2 is CH=CH_2]
Found in Haemoglobin
and Myoglobin



Chlorophyll a (R=CH_3)
Chlorophyll b (R=CHO)

Structures of some important compounds mentioned in Section 10.8

coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be precipitated from this solution by the addition of Zinc.

- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.
- There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by the chelating ligands D-penicillamine and desferrioxime B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: cis-platin and related compounds.
- Billions of dollars at the international level are generated by industrial processes using organometallic compounds as catalysts. These catalysts are either of the homogeneous type (soluble in the reaction medium) or of the heterogeneous type (insoluble in the reaction medium). The catalysed polymerisation of alkenes at atmospheric pressure and ambient temperature using Ziegler-Natta catalyst (titanium tetrachloride plus triethylaluminium) is one of the great discoveries of organometallic chemistry. The first effective homogeneous catalyst chlorotris(triphenylphosphine)rhodium(I), $[RhCl(PPh_3)_3]$ for hydrogenation was given by Wilkinson. It is visualised that organometallics will play an everexpanding role in the production of pharmaceuticals, agrochemicals, flavours, fragrances, semi-conductors and ceramic precursors in the future.
- These days, new drugs are being created by derivitisation with metallocene groups to create new potent agents for biomedical applications.

SUMMARY

Coordination chemistry, which is also central to organometallics and bio-inorganics, is an important, ever-expanding and challenging area of modern inorganic chemistry. During the last fifty years, advances in this area, have provided: i) development of new concepts and models of bonding and molecular structure, ii) novel breakthroughs in chemical industry, and iii) vital insights into the functioning of critical components of biological systems.

The first systematic attempt at explaining the formation, reactions, structure and bonding of a coordination compound was made by A. Werner. His theory postulated the use of two types of linkages (primary and secondary), by a metal atom/ion in a coordination compound. In the modern language of chemistry these linkages are recognized as the ionizable (ionic) and non-ionizable (covalent) bonds, respectively. Using the property of isomerism, Werner predicted the geometrical shapes of a large number of coordination entities.

The Valence Bond Theory (VBT) was extended to coordination compounds by Linus Pauling in 1931. It explains with reasonable success, the formation, magnetic nehaviour and geometrical shapes of coordination compounds. It, however, fails to provide a quantitative interpretation of magnetic behaviour and has nothing to say about the optical properties of these compounds.

The extension of Crystal Field Theory (CFT) to coordination compounds is based on the effect of different crystal fields (provided by the ligands taken as point charges), on the degeneracy of *d* orbital energies of the central metal atom/ion). The splitting of the *d* orbitals, provides for different electronic arrangements in strong and weak crystal fields. The treatment provides for quantitative estimations of orbital separation energies, magnetic moments and spectral and stability parameters. However, the assumption that ligands constitute point charges creates many theoretical difficulties.

An organometallic compound, by definition, must have at least one metal-carbon bond. Broadly organometallics are classified into: a) organometallics of main group elements and b) *d*- and *f*-block organometallics. The *s*-block organometallics of Li, Be, Mg have polar M-C bonds, while those of the heavier metals are even more ionic. The *p*-block organometallics are covalent compounds.

The first *d*-block organo metallic compound $[PtCl_3(C_2H_4)]^-$; was prepared by Zeise. This was followed by preparation of $[Ni(CO)_4]$ and a variety of metal carbonyl clusters. **Metal carbonyls find use as industrial catalysts and precursors in organic synthesis**. The bonding of carbon monoxide to a metal atom/ion is a combination of a σ bond (ligand to metal) and a π bond (metal to ligand). This unique synergic bonding provides stability to metal carbonyls. The synthesis of **ferrocene** in 1951 ushered in a new dimension in organometallic chemistry based on the concept of pi-bonding of carbocyclic rings to metal atoms. Collectively, such compounds are called **metallocenes**.

EXERCISES

10.1 Define the terms: coordination entity, central metal, ligand, donor atom, coordination number and oxidation number.

10.2 What is meant by the denticity of a ligand? Give examples of a unidentate and a didentate ligand.

10.3 Which postulates did Werner use to explain the bonding in coordination compounds? What is the main weakness of Werner's theory?

10.4 What is understood by: a) a chelating ligand, b) an ambidentate ligand? Answer using specific examples.

10.5 Complete the following statements for the coordination entity (complex ion) $[CrCl_2(ox)_2]^{3-}$:
(a) ox is abbreviation for.....
(b) The oxidation number of chromium is.....
(c) The coordination number of chromium is.....
(d) .....is a didentate ligand.

10.6 Specify the oxidation numbers of the metals in the following coordination entities:
(a) $[Co(CN)(H_2O)(en)_2]^{2+}$ (b) $[PtCl_4]^{2-}$ (c) $[CrCl_3(NH_3)_3]$ (d) $[CoBr_2(en)_2]^+$
(e) $K_3[Fe(CN)_6]$.

10.7 Using IUPAC norms write the formulae for the following:
(a) Tetrahydroxozincate (II)
(b) Hexaamine cobalt (III) sulphate
(c) Potassiumtetrachloropalladate(II)
(d) Potassium tri(oxalato)chromate(III)
(e) Diamminedichloroplatinum(II)
(f) Hexaammineplatinum (IV)
(g) Potassium tetracyanonickelate(II)
(h) Tetrabromocuprate(II)
(i) Pentaamminenitrito-O-cobalt(III)
(j) Pentaamminenitrito-N-cobalt(III).

10.8 Using IUPAC norms write the systematic names of the following:
(a) $[Co(NH_3)_6]\ Cl_3$
(b) $[CoCl(NO_2)(NH_3)_4]Cl$
(c) $[Ni(NH_3)_6]Cl_2$
(d) $[PtCl(NH_2CH_3)(NH_3)_2]Cl$
(e) $[Mn(H_2O)_6]^{2+}$
(f) $[Co(en)_3]^{3+}$
(g) $[Ti(H_2O)_6]^{3+}$
(h) $[NiCl_4]^{2-}$
(i) $[Ni(CO)_4]$

10.9 Explain with examples geometric and optical isomerism in coordination compounds.

10.10 Specify which out of the following complex structures exhibit geometric isomerism:
(a) linear (b) square-planar (c) tetrahedral (d) octahedral.

10.11 How many geometric isomers are possible in the following coordination entities:
(a) $[Cr(ox)_3]^{3-}$ (b) $[CoCl_3(NH_3)_3]$

10.12 Draw the structures of optical isomers of:
(a) $[Cr(ox)_3]^{3-}$ (b) $[PtCl_2(en)_2]^{2+}$ (c) $[CrCl_2(en)(NH_3)_2]^+$

10.13 Draw all the isomers (geometric and optical) of:
(a) $[CoCl_2(en)_2]^+$ (b) $[CoCl(en)_2(NH_3)]^{2+}$ (c) $[CoCl_2(en)(NH_3)_2]^+$

10.14 Draw the structures of:
(a) Cis-dichlorotetracyanochromate(III)
(b) Mer-triamminetrichlorocobalt(III)
(c) Fac-triaquatrinitro-N-cobalt(III).

10.15 Illustrate with an example each of the following:
(a) ionization isomerism
(b) linkage isomerism
(c) coordination isomerism.

10.16 Sketch the geometrical shapes of the following sets of hybrid orbitals:
(a) dsp^2 (b) dsp^3 (c) d^2sp^3 (d) sp^3

10.17 Explain on the basis of valence bond theory, the experimental findings that $[Ni(CN)_4]^{2-}$ ion with a square-planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

10.18 Write the correct formulae for the following coordination compounds:
(a) $CrCl_3.6H_2O$ (violet, with 3 chloride ions/unit formula)
(b) $CrCl_3.6H_2O$ (light green colour, with 2 chloride ions/unit formula)
(c) $CrCl_3.6H_2O$ (dark green colour, with 1 chloride ion/unit formula)
[Hint: some of these compounds may exist as hydrates].

10.19 Aqueous copper sulphate solution (blue in colour] gives: a) a green precipitate with aqueous potassium fluoride, and (b) a bright green solution with aqueous potassium chloride. Explain these experimental results.

10.20 What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S(g)$ is passed through this solution?

10.21 Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory: (a) $[Fe(CN)_6]^{4-}$ (b) $[FeF_6]^{3-}$ (c) $[Co(ox)_3]^{3-}$ (d) $[CoF_6]^3$.

10.22 Write the valence bond description of: (a) $[Ni(CN)_4]^{2-}$ (b) $[Ni\ Cl_4]^{2-}$.

10.23 What is understood by the generalization, 'magnetic criteria of the bond type'? Illustrate your answer with suitable examples.

10.24 Draw figure to show splitting of degenerate *d* orbitals in an octahedral crystal field.

10.25 State the essential requirements for regarding a compound as an organometallic. Which amongst the following are organometallic compounds:
(a) $B(CH_3)_3$ (b) $B(OCH_3)_3$ (c) $SiCl_3(CH_3)$ (d) $N(CH_3)_3$

10.26 Write the formulae of the following:
(a) methyllithium
(b) tetramethylsilane
(c) trimethylbiemuth
(d) trimethylarsane
(e) hexamethyldialuminium
(f) trimethylboron.

10.27 Sketch the structures of the organometallic compounds given in question10.26.

10.28 Give IUPAC name and draw the structures of:
(a) $Ni(CO)_4$ (b) $Fe(CO)_5$ (c) $[PtCl_3(C_2H_4)]^-$ (d) $[Cr(CO)_6]$.

10.29 Assign oxidation number to the metal atom in the compounds given in question 10.28.

10.30 Discuss the nature of bonding in $[Ni(CO)_4]$.

10.31 Discuss briefly the role of coordination compounds in: (a) biological systems, (b) analytical chemistry, (c) medicinal chemistry, and (d) extraction/metallurgy of metals.

UNIT 11

NUCLEAR CHEMISTRY

OBJECTIVES

After studying this Unit, you will be able to:

- know about radioactivity and nature of different types of radiations.
- learn about the radioactive decay series.
- define nuclear binding energy and rate of radioactive decay.
- know about artificial nuclear reactions and synthetic elements.
- learn about nuclear fission, principle of nuclear and breeder reactors.
- know about nuclear fusion reactions
- learn about applications of radioisotopes including radio-carbon dating.

"If the radiance of a thousand suns were to burst into the sky, that would be like the splendour of the Mighty One."

– Bhagvad Gita

Chemistry is mostly concerned with extra nuclear atomic structure rather than the nucleus. Nevertheless, there are many aspects of nuclear science that are important to chemistry. Nuclear chemistry is concerned with nuclear stability and the process of nuclear changes. Examples of these processes are radioactivity, artificial transmutations, nuclear fission and nuclear fusion. The energies involved in some of these processes are million times greater than those in ordinary chemical reactions. In this Unit, we shall deal with some important aspects of nuclear chemistry.

11.1 THE NUCLEUS

An atom of any element consists of a positively charged nucleus surrounded by one or more negatively charged electrons, the whole atom as such being electrically neutral. Nearly all the mass of an atom is concentrated in the nucleus, which has a radius of about 10^{-15} m, i.e., about 10^{-5} times that of the atom. The nucleus consists of positively charged *protons* and electrically neutral *neutrons*, collectively known as *nucleons*. The atomic number, Z of an atom is the number of protons in the nucleus that defines the identity of an atom. The *mass number*, A, of an atom is the integer nearest to the relative atomic mass and is equal to the number of nucleons in the nucleus; it follows that the number of neutrons in the same nucleus is A-Z. A particular nuclear species with a specific atomic number and a mass number is referred to as, *nuclide*. Nuclides of the same element of different mass numbers are called *isotopes* of that element.

11.2 DISCOVERY OF RADIOACTIVITY AND NATURE OF RADIATIONS

The phenomenon of radioactivity was accidentally discovered by French scientist Henri Becquerel, who in 1896 reported that uranium salts emitted a radiation with properties similar to X-rays (discovered earlier by Röntgen, 1895). Investigations of Pierre and Marie Curie in later years led to the discovery that the atoms of certain other elements such as thorium, radium and polonium undergo spontaneous decay and emit similar radiations. These elements are said to be *radioactive* and the phenomenon is known as *radioactivity*. Three types of radiation from recognised radioactive elements are, *α-particles* (helium nuclei), *β-particles* (electrons of nuclear origin having high kinetic energy) and *γ-radiation* (high frequency radiation). It was realized that *radioactivity of an element is independent of its physical state, its chemical environment or temperature, suggesting that it is a property of nucleus.*

Rutherford studied the penetrating power of these radiations and their behaviour in electric and magnetic field. His conclusions are summarized below:

(a) Alpha (α) particles are fast moving helium nuclei (He^{2+} or ^4_2He) with energy about $(6 - 16)\times10^{-13}$ J. They penetrate a few centimeters of air causing ionization of some molecules but they are stopped by a few sheets of paper or a very thin metal foil.

(b) Beta (β^-) Particles are fast moving electrons. Their energies are about $(0.03 - 5.0) \times 10^{-13}$ J, but since they are much lighter than α-particles, they travel much faster and have a range of penetration of 1-2 m in air. Their total ionizing effect is about the same as that of α-particles but it is effective over much longer distances.

(c) Gamma (γ) radiation is a very short wavelength (and therefore very high energy) radiation that often accompanies α or β^- emission. It has great penetrating power and is stopped only by a thickness of about 15-20 cm of lead. On passage through matter they are capable of ejecting high-speed electrons.

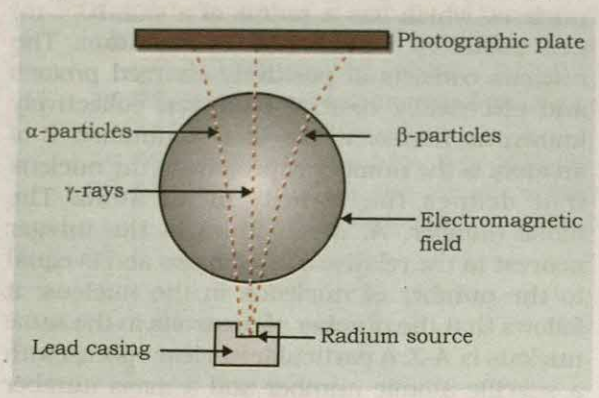


Fig. 11.1 *Radiation from a radioactive element radium and the effect of a magnetic field on the same.*

The effect of a magnetic field on the radiation obtained from radium is shown in Fig. 11.1.

11.2.1 Group Displacement Law

The chemical consequences of radioactive decay may be summarised as follows:

Emission of an α-particle (a helium nucleus) lowers the atomic number by two and mass number by four; emission of a β^--particle (an electron of nuclear origin) raises the atomic number by one and leaves the mass number unchanged. Thus, the new element may be displaced either to the left (two places in case of α-emission) or to the right (one place in case of β^--emission) in the periodic table. This displacement is known as *Group Displacement Law*. The emission of γ-radiation affects neither atomic number nor mass number. The new element formed in this way is usually known as the *daughter element* and the one that has undergone decay, the *parent element*. For example, the decay of $^{238}_{92}U$ nucleus by an α-particle emission produces a thorium nucleus $^{234}_{90}Th$. This nuclear reaction is represented by the equation:

$$^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He$$

It may be pointed out that there is a conservation of both atomic number and mass number in the equation of a nuclear reaction.

In case an α-emission is followed by two successive β^--emissions, a nuclide which is isotopic with the original one may be produced, e.g.,

$$^{238}_{92}U \xrightarrow{-\alpha} {}^{234}_{90}Th \xrightarrow{-\beta} {}^{234}_{91}Pa \xrightarrow{-\beta} {}^{234}_{92}U$$

The nuclides having same mass numbers but different atomic numbers such as $^{234}_{90}Th$, $^{234}_{91}Pa$, and $^{234}_{92}U$ are known as *isobars*.

In addition to α, β^- and γ emissions, two other types of decay processes are also observed, viz. *β^+ emission* and *K-capture*.

β^+ emission – A positively charged beta particle (β^+) is known as *positron*. The emission of a positron (β^+) results into a decrease of atomic number by one unit. It is now believed that β-emission involves the transformation within the nucleus of a neutron to proton or proton to neutron. Thus

$$n \rightarrow p^+ + \beta^- \; ; \; p^+ \rightarrow n + \beta^+$$

An example of β^+ emission is

$$^{22}_{11}Na \rightarrow {}^{22}_{10}Ne + {}^{0}_{+1}e(\beta^+)$$

***K*-capture** – In some nuclides, the nucleus may capture an electron from the *K* shell. The vacancy created is filled by electrons from higher levels giving rise to characteristic X-rays. This process is known as *K-electron capture* or simply *K-capture*. An example of *K*-capture is:

$$^{133}_{56}Ba + e^- \rightarrow {}^{133}_{55}Cs + X\text{-ray}$$

The change in the nucleus is represented by $p^+ + e^- \rightarrow n$; the neutron produced remains in the nucleus and the atomic number decreases by one unit as a result of *K*-capture.

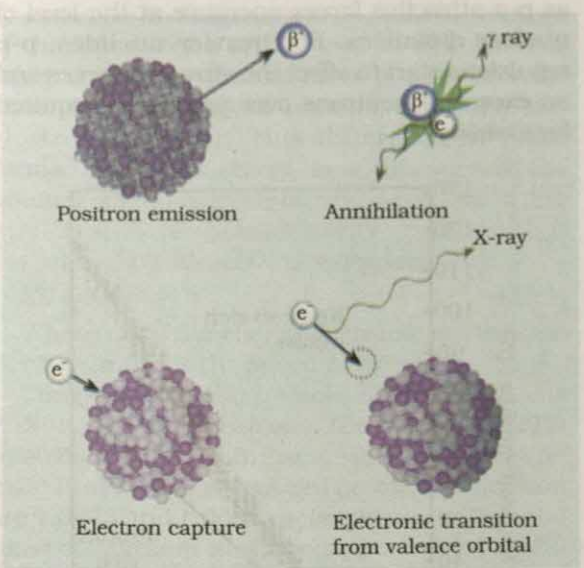


Fig. 11.1(a) *β^+- emission and K-capture of electron.*

Example 11.1
What may be the place of a daughter element in the periodic table, which is obtained after the nuclide $^{218}_{84}Po$ undergoes an α emission followed by two successive β emissions?

Solution
The loss of one α particle will reduce the mass number by four and atomic number by two. Subsequent two β^- emissions will increase the atomic number by two without affecting the mass number. Hence, the new element will be only an isotope of the parent nuclide with mass number four less, i.e., $^{214}_{84}Po$ and hence its position in the periodic table remains unchanged.

$$^{218}_{84}Po \xrightarrow{-\alpha} {}^{214}_{82}Pb \xrightarrow{-\beta} {}^{214}_{83}Bi \xrightarrow{-\beta} {}^{214}_{84}Po$$

11.2.2 Radioactive Decay Series

Radioactive heavy nuclei decay by a series of α- and/or β^--emissions, finally resulting in the formation of a stable isotope of lead. All the nuclei formed from initial to the final stable element constitute a *series*. There are four decay series distinguished by whether the mass numbers are divided by 4 or whether when divided by four, there are remainders of 1, 2, or 3. The parent of (4n) is $^{232}_{90}Th$ and its end product is $^{208}_{82}Pb$. The corresponding parents of the (4n + 2) and (4n + 3) series are $^{238}_{92}U$ and $^{235}_{92}U$, respectively. An artificial series (4n + 1) starts with Plutonium, $^{241}_{94}Pu$ and ends in $^{209}_{83}Bi$. These series are summarized in Table 11.1.

As an illustration, the complete uranium decay series is given on next page and schematically presented further in Fig. 11.2.

Table 11.1 The Decay Series

Series	Name of the Series	Parent Element	End Stable Element	Value of n for the Parent Element	Value of n for the End Element
4n	Thorium series	Thorium–232	Lead–208	58	52
4n + 1	Neptunium	Plutonium–241	Bismuth–209	60	52
4n + 2	Uranium series	Uranium–238	Lead–206	59	51
4n + 3	Actinium	Uranium–235	Lead–207	58	51

$$^{238}_{92}U \xrightarrow{-\alpha} {}^{234}_{90}Th \xrightarrow{-\beta} {}^{234}_{91}Pa \xrightarrow{-\beta} {}^{234}_{92}U \xrightarrow{-\alpha} {}^{230}_{90}Th \xrightarrow{-\alpha} {}^{226}_{88}Ra \xrightarrow{-\alpha} {}^{222}_{86}Rn \xrightarrow{-\alpha} {}^{218}_{84}Po \xrightarrow{-\alpha} {}^{214}_{82}Pb \xrightarrow{-\beta} {}^{214}_{83}Bi \xrightarrow{-\beta} {}^{214}_{84}Po \xrightarrow{-\alpha} {}^{210}_{82}Pb \xrightarrow{-\beta} {}^{210}_{83}Bi \xrightarrow{-\beta} {}^{210}_{84}Po \xrightarrow{-\alpha} {}^{206}_{82}Pb$$

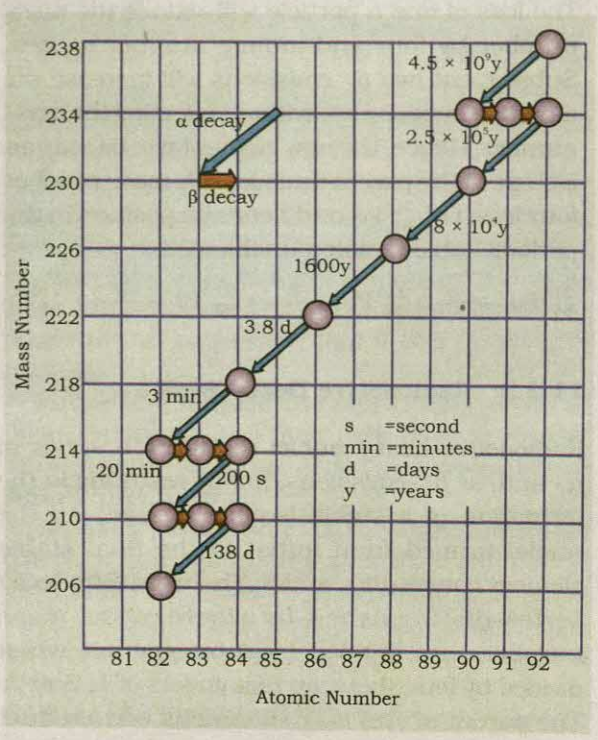


Fig. 11.2 *The Uranium-238 series. The times are the half-lives of the nuclides.*

Example 11.2

In the decay series $^{238}_{92}U$ to $^{206}_{82}Pb$, how many α-particles and how many β^- -particles are emitted?

Solution

The change in mass is 238 – 206 = 32 units. It means that 32 / 4 = 8 α-particles are emitted. With the emission of 8 α-particles, the change in atomic number will be 8 × 2 = 16, i.e., the new element would have atomic number 92 – 16 = 76. But the final product Pb, has atomic number 82. It means there would have been an emission of 82 – 76 = 6 β^- particles.

11.2.3 Nuclear Stability and Neutron/ Proton ratio

A plot of *N* (the neutron number) against *Z* (atomic number or number of protons) is shown in Fig. 11.3. From this, it is clear that for stable nuclides up to *Z*=20, *N*= 20 (^{40}Ca), the relationship can be represented by a line with a slope of 45 degree, i.e., the maximum stability is attained when *N* = *Z*. At higher values of *Z*, the graph becomes curved with the slope of the curve gradually increasing. To the right of curve where the *N*/*Z* ratio is lower than that required for stability, a radioactive nuclide can decay by β^+ emission or *K*-electron capture, which produces a daughter nucleus with a ratio of (*N*+ 1)/ (*Z*- 1). To the left of the curve, a radioactive nuclide would be neutron rich and would decay by β^- emission to produce a daughter nucleus with a lower *N*/*Z* ratio of (*N* – 1)/ (*Z*+ 1). In either case, the daughter nuclide might be stable (i.e., have *N*/*Z* ratio within the stable range) or undergo further decay until stability is attained. This behaviour is explained by the strong n-p as well as p-p attractive forces operative at the level of nuclear distances. For heavier nuclides, p-p repulsions start to offset the attractive forces and an excess of neutrons over protons is required for stability.

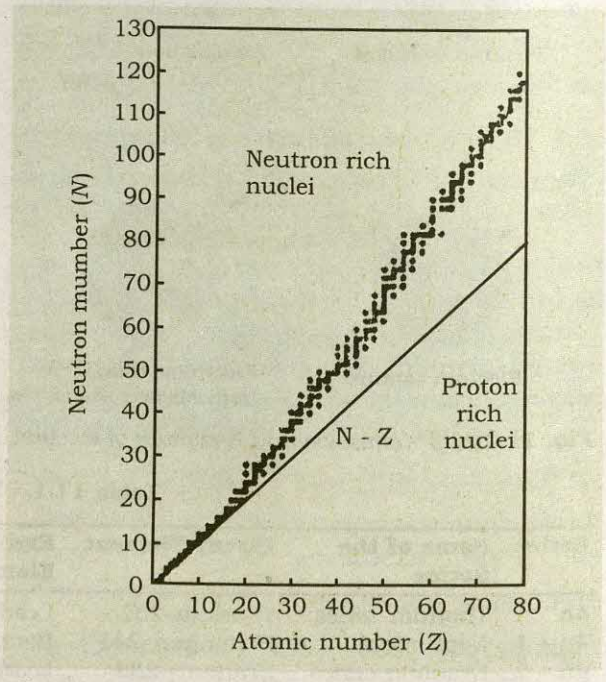


Fig. 11.3 *A plot of number of neutrons (N) against the atomic number (Z) for a range of stable nuclei.*

When the value of Z becomes greater than 82 some nuclides attain greater stability (i.e. decay by α-emission) which reduces the initial N/Z value to $(N-2)/(Z-2)$, the more important consequence being the reduction of Z leading to the reduction of p-p repulsions.

From the above discussion, it appears that, the neutron-proton ratio plays a vital role in deciding the stability of nuclides as also the kinds of decay they undergo.

Example 11.3

What may be the new neutron and proton ratio after a nuclide, $^{238}_{92}U$ loses an α-particle?

Solution

If the original neutron-proton ratio was N/Z (146/92), the new ratio will be (*N*-2)/ (*Z*-2), i.e., 144/90.

11.2.4 Nuclear Binding Energy

The mass of hydrogen atom is equal to the sum of the masses of a proton and an electron. For other atoms, the atomic mass is less than the sum of the masses of protons, neutrons and electrons present. This difference in mass termed as, *mass defect*, is a measure of the *binding energy* of protons and neutrons in the nucleus. The mass-energy relationship postulated by Einstein is expressed as:

$$\Delta E = \Delta m c^2 \qquad (11.1)$$

Where ΔE is the energy liberated, Δm the loss of mass and c is the speed of light.

Consider the helium nucleus which contains 2 protons and 2 neutrons; the mass of helium nucleus on ^{12}C =12 m_u, scale is 4.0017 m_u. The masses of individual isolated proton and neutron are 1.0073 and 1.0087 m_u respectively. The total mass of 2 protons and 2 neutrons is $(2 \times 1.0073) + (2 \times 1.0087 = 4.0320\ m_u$. The loss in mass or mass defect for helium nucleus is

$$4.0320 m_u - 4.0017 m_u = 0.0303\ m_u$$

Since $1 m_u = 1.66057 \times 10^{-27}$ kg and

$c = 2.998 \times 10^8$ ms^{-1}

$\Delta E = 0.0303 \times 1.66057 \times 10^{-27} \times 6.02 \times 10^{23} \times (2.998 \times 10^8)^2$ kg m^{2}s^{-2} mol^{-1}

$= 2.727 \times 10^{12}$ J mol^{-1}

Thus, the **molar** nuclear binding energy of helium nucleus, ^{4}He, is 2.73×10^{12} J mol^{-1}.

Binding energy of a nucleus is generally quoted as energy in million electron volts (MeV) per nucleon. One million electron volts are equivalent to 9.6×10^{10} J mol^{-1}. Thus, the formation of helium nucleus results in the release of $2.7 \times 10^{12}/9.6 \times 10^{10}$ MeV = 28 MeV (approximately).

In comparing the binding energies of different nuclei, it is more useful to consider the binding energy per nucleon. For example, helium nucleus contains 4 nucleons (2 protons and 2 neutrons), the binding energy per nucleon in this case is 28/4 = 7 MeV.

Binding energies of the nuclei of other atoms can be calculated in a similar manner. Fig. 11.4 shows the binding energies of the nuclei of atoms plotted against their respective mass number. Three features of interest may be noted in this figure. First, nuclei with mass number around 60 have the highest binding energy per nucleon. Second, species of mass numbers 4, 12, and 16 have high binding energy per nucleon implying that the nuclei ^{4}He, ^{12}C, and ^{16}O. are particularly stable. Third, the binding energy per nucleon decreases appreciably above mass number 100.

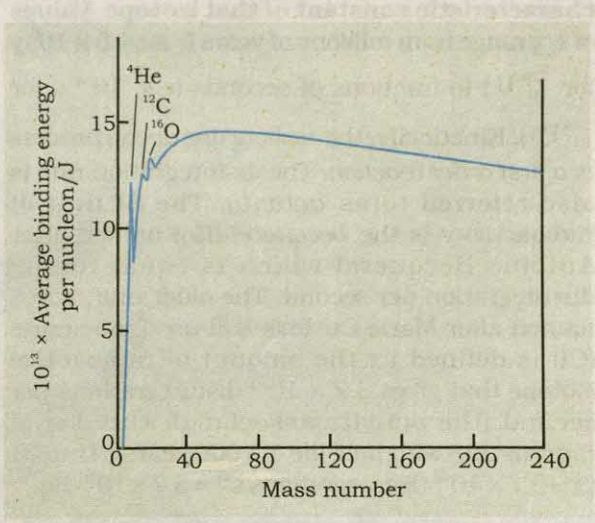


Fig. 11.4 *A plot of nuclear binding energy per nucleon against the mass number for naturally occurring nuclides.*

The form of relationship between, binding energy per nucleon and mass number indicates that heavy nuclei would release mass (and therefore energy) on division (or fission) into two

nuclei of medium mass and that the light nuclei would release mass (and therefore energy) on fusion to form heavier nuclei. These processes called *fission* and *fusion* are described later in this Unit.

11.2.5 Rate of Radioactive Decay

The decay of a radioactive element is a random process and is independent of external factors such as temperature and environmental changes. The rate of decay of a nucleus follows the natural exponential law (first order kinetics, Unit 6) and if the number of parent nuclide present at any time is N_o and the number of nuclei after time (t) in seconds is N_t, then

$$N_t = N_o e^{-kt} \qquad (11.2)$$

Where k is the radioactive decay constant for a particular nuclear species. The duration of time during which half of the nuclei originally present decay is called the *half-life* of the isotope. Thus, $N_t = ½ N_o$ and its relationship to k is obtained as follows:

$$e^{-kt} = N_t / N_o = ½$$
$$k\, t_{1/2} = \ln 2$$
$$\therefore\ t_{1/2} = (\ln 2) / k = 0.693 / k \qquad (11.3)$$

where $t_{1/2}$ is the half-life period. **The half-life of a particular radioactive isotope is a characteristic constant of that isotope.** Values of $t_{1/2}$ range from millions of years (e.g., 4.5×10^9 y for $^{238}_{92}U$) to fractions of seconds (e.g. 10^{-4} s for $^{214}_{84}Po$). Kinetically, the *radioactive decay process is a first order reaction.* The disintegration rate is also referred to as *activity*. The SI unit of radioactivity is the *becquerel* (Bq) named after Antoine Becquerel which is equal to one disintegration per second. The older unit, *curie*, named after Marie Curie is still used; one curie (Ci) is defined as the amount of radioactive isotope that gives 3.7×10^{10} disintegrations per second (the activity associated with 1 g of radium-225 with half-life of 1600 years). Thus, 1 Ci = 3.7×10^{10} disintegrations s^{-1} = 3.7×10^{10} Bq.

Example 11.4
The atomic mass of ^{19}F is 18.9984 m_u. If the masses of proton and neutron are 1.0078 m_u and 1.0087 m_u, respectively, calculate the binding energy per nucleon (ignore the mass of electrons). (1 m_u = 931 MeV)

Solution
Mass defect
= [{ $(9 \times 1.0078) + (10 \times 1.0087)$} – 18.9984]$m_u$
= 0.1588 m_u
Binding energy per nucleon
= (0.1588 × 931) MeV/ 19
= 7.78 MeV

Example 11.5
Calculate $t_{1/2}$ for ^{241} Am in years given that it emits 1.2×10^{11} α-particles per gram per second.

Solution
1 gram of Am contains N_A / 241 nuclei = N_o, using the equation
Rate of decay = 1.2×10^{11} g^{-1} s^{-1}
$= k \times N_o = k \times N_A$ / 241
$= k \times 6.02 \times 10^{23}$ /241
$k = 1.2 \times 10^{11} \times 241$ / 6.02×10^{23}
$= 4.8 \times 10^{-11}$ s^{-1}
and $t_{1/2} = \ln 2/k = 0.693/k$
$t_{1/2} = 0.693 / (4.8 \times 10^{-11}\ s^{-1})$
$= 1.44 \times 10^{10}$ s = 462.9 years.

11.3 ARTIFICIAL NUCLEAR REACTIONS

The first artificial transmutation was carried out by Rutherford in 1919 who bombarded nitrogen gas with alpha particles and obtained hydrogen and oxygen,

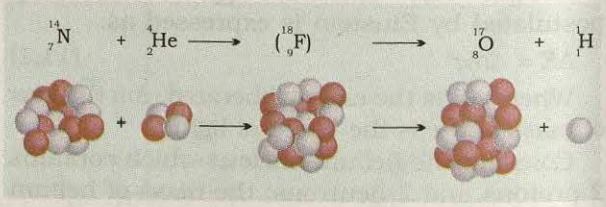


Fig. 11.4 *(a) Artificial transmutation.*

The isotope $^{17}_{8}O$ and $^{1}_{1}H$ are stable and no further disintegration takes place. Charged particles such as α-particles, deuterons (heavy hydrogen isotope, $^{2}_{1}D$), protons, and electrons can be accelerated to very high speeds by fluctuating electric and magnetic fields in machines such as *cyclotron*, *synchrotron*, etc. (Fig. 11.5). These high-speed particles are more efficient in causing nucleus to disintegrate on impact. Some typical transmutations involving various particles are summarised below:

(1) *Alpha particle induced reactions*

$$^{9}_{4}Be + ^{4}_{2}He \rightarrow ^{12}_{6}C + ^{1}_{0}n$$

Since α-particle is used and a neutron is produced, the reaction may be termed as (α, n) reaction. In another α-bombardment nuclear reaction, the isotope produced is itself radioactive. Thus,

$$^{27}_{13}Al + ^{4}_{2}He \rightarrow ^{30}_{15}P + ^{1}_{0}n$$

The isotope $^{30}_{15}P$ undergoes decay by positron (β^+) emission:

$$^{30}_{15}P \rightarrow ^{30}_{14}Si + \beta^+$$

This was the first example of radioactivity produced by artificial means.

(2) *Deuteron- induced reactions:*

(i) $^{12}_{6}C + ^{2}_{1}H \rightarrow ^{13}_{7}N + ^{1}_{0}n$, (D,n) reaction

(ii) $^{16}_{8}O + ^{2}_{1}H \rightarrow ^{14}_{7}N + ^{4}_{2}He$, (D,α) reaction

(3) *Proton-induced reactions:*

(i) $^{14}_{7}N + ^{1}_{1}H \rightarrow ^{15}_{8}O + \gamma$, (p,γ) reaction

(ii) $^{7}_{3}Li + ^{1}_{1}H \rightarrow ^{4}_{2}He + ^{4}_{2}He$ (p,α) reaction

(4) *Neutron-induced reactions:*

(i) $^{23}_{11}Na + ^{1}_{0}n \rightarrow ^{24}_{11}Na + \gamma$, (n,γ) reaction

(ii) $^{131}_{52}Te + ^{1}_{0}n \rightarrow ^{132}_{53}I + ^{0}_{1}e$, (n,$\beta^-$) reaction

(iii) $^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}H$, (n,p) reaction

Some of the isotopes produced as a result of neutron bombardment find applications in different areas (see later uses of radioisotopes). The preparation of isotopes of elements beyond uranium involves many neutron-induced reactions.

Example 11.6

What do you understand by the following notations in respect of the types of artificial transmutations?

(i) (n, β^-) (ii) (p, β^-) (iii) (α, n) and (iv) (D, p)

Solution

(i) The striking particle is n and the particle in the product is β^-.

(ii) The striking particle is p (proton), the particle produced is β^-.

(iii) The striking particle is α-particle ($^{4}_{2}He$) and one neutron is on the product side.

(iv) Deuteron ($^{2}_{1}H$) is the striking particle and one proton is in the product.

11.4 SYNTHETIC ELEMENTS INCLUDING TRANSURANICS

Nuclear reactions involving the bombardment technique by different particles have been used to synthesise artificial elements such as technetium, astatine, and transuranium

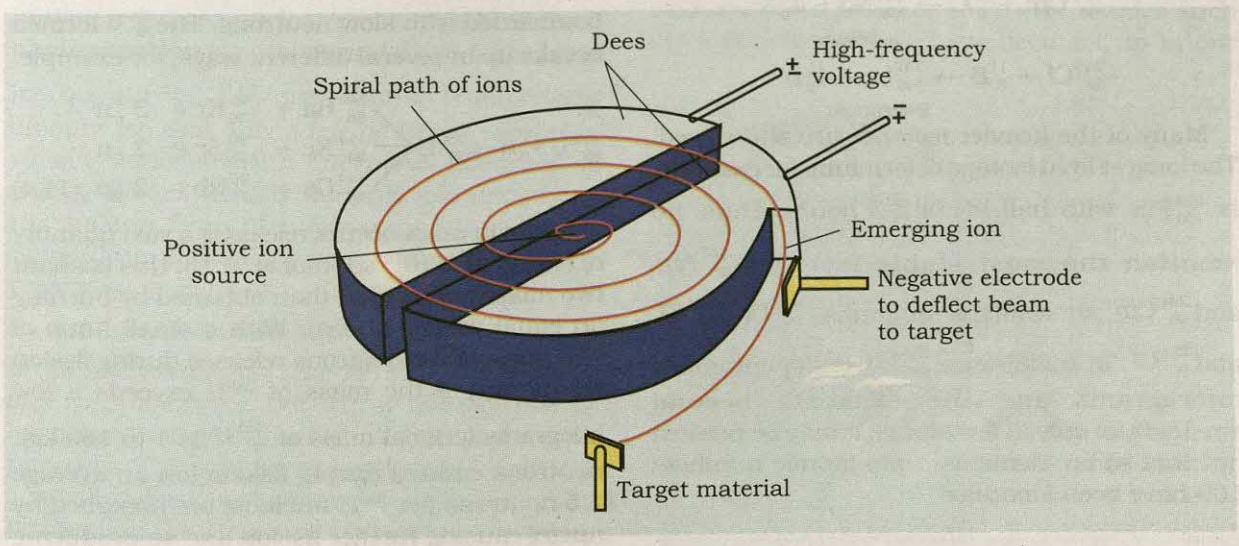


Fig. 11.5 *A Cyclotron. Positive ions are introduced at the centre of the cyclotron. Attraction of the ions will be crossing the gap between the dees when the electric polarities are just right to accelerate them. Magnet poles above and below the dees produce a magnetic field that keepthe ions moving in a spiral path and at the end of their path, the ions encounter a negative electrode that deflects them to a target material.*

elements (i.e., elements beyond $Z > 92$) which follow uranium in the periodic table. The nuclear reactions which are employed to synthesise some of these elements are given below.

(1) *Technetium:*

$$^{96}_{42}Mo + {}^{2}_{1}H \rightarrow {}^{97}_{43}Tc + {}^{1}_{0}n$$

(2) *Neptunium and plutonium:*

$$^{238}_{92}U + {}^{1}_{0}n \rightarrow {}^{239}_{92}U + \gamma$$

$$^{239}_{92}U \xrightarrow{-\beta^-} {}^{239}_{93}Np \xrightarrow{-\beta^-} {}^{239}_{94}Pu$$

$^{239}_{94}Pu$ is an α-emitter with half-life of 2.4×10^4 years.

(3) *Americium and curium*

$$^{239}_{94}Pu + {}^{1}_{0}n \rightarrow {}^{240}_{94}Pu + \gamma$$

$$^{240}_{94}Pu + {}^{1}_{0}n \rightarrow {}^{241}_{94}Pu + \gamma$$

$$^{241}_{94}Pu \rightarrow \underset{\text{americium}}{^{241}_{95}Am} + \beta^-$$

$$^{239}_{94}Pu + {}^{4}_{2}He \rightarrow \underset{\text{curium}}{^{242}_{96}Cm} + {}^{1}_{0}n$$

(4) *Berkelium and californium:*

$$^{241}_{95}Am + {}^{4}_{2}He \rightarrow {}^{243}_{97}Bk + 2{}^{1}_{0}n$$

$$^{242}_{96}Cm + {}^{4}_{2}He \rightarrow {}^{245}_{98}Cf + {}^{1}_{0}n$$

(5) *Later elements*

Bombardment with heavier nuclides produces later elements. For example:

$$^{246}_{96}Cm + {}^{12}_{6}C \rightarrow \underset{\text{nobelium}}{^{254}_{102}No} + 4{}^{1}_{0}n$$

$$^{250}_{98}Cf + {}^{11}_{5}B \rightarrow \underset{\text{lawrencium}}{^{257}_{103}Lr} + 4{}^{1}_{0}n$$

Many of the heavier isotopes are short lived. The longest lived isotope of fermium, for example, is $^{254}_{100}Fm$ with half-life of 3.3 hours. Thus, (to mention the most stable isotopes) $^{241}_{95}Am$ and $^{244}_{96}Cm$ are available in grams, $^{249}_{97}Bk$, $^{249}_{98}Cf$ and $^{251}_{98}Cf$ in milligrams, $^{253}_{99}Es$ (einsteinium) in micrograms and the elements beyond einsteinium only in few atoms. It may be pointed out that so far elements, upto atomic numbers 109 have been identified.

Example 11.7

In artificial transmutation which has stronger striking ability and why, proton or neutron moving with the same speed?

Solution

Neutron with its neutral character has stronger striking ability in nuclear reactions. Proton with positive charge is not so effective to attack the positively charged nucleus.

Example 11.8

Complete the following nuclear equations:

(i) $^{246}_{96}Cm + {}^{12}_{6}C \rightarrow {}^{254}_{102}No + ...$

(ii) $^{239}_{94}Pu + ... \rightarrow {}^{242}_{96}Cm + {}^{1}_{0}n$

Solution

(i) $^{246}_{96}Cm + {}^{12}_{6}C \rightarrow {}^{254}_{102}No + 4{}^{1}_{0}n$

(ii) $^{239}_{94}Pu + {}^{4}_{2}He \rightarrow {}^{242}_{96}Cm + {}^{1}_{0}n$

11.5 NUCLEAR FISSION

Two consequences of nuclear reactions, phenomena of *nuclear fission* and *nuclear fusion*, are important from the point of view of harnessing nuclear energy for peaceful or destructive purposes.

In a **nuclear fission** reaction, a heavy nucleus splits up into two main fragments of lighter nuclei and several neutrons. Of the three natural isotopes of uranium ($^{238}_{92}U$, $^{235}_{92}U$, and $^{234}_{92}U$, the $^{235}_{92}U$ nucleus undergoes nuclear fission when bombarded with slow neutrons. The $^{236}_{92}U$ formed breaks up in several different ways, for example:

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{236}_{92}U \begin{cases} \rightarrow {}^{140}_{56}Ba + {}^{93}_{36}Kr + 3\,{}^{1}_{0}n \\ \rightarrow {}^{144}_{54}Xe + {}^{90}_{38}Sr + 2\,{}^{1}_{0}n \\ \rightarrow {}^{144}_{55}Cs + {}^{90}_{37}Rb + 2\,{}^{1}_{0}n \end{cases} \quad (11.4)$$

A loss in mass occurs releasing a vast quantity of energy (2×10^{10} kJ/mol of ^{235}U): this is about two million times that than obtained by burning an equal weight of coal. With a small lump of ^{235}U, most of the neutrons released during fission escape but if the mass of ^{235}U exceeds a few kilograms (critical mass of $^{235}_{92}U$ is 1 to 100 kg), neutrons emitted during fission (on an average 2.5 neutrons per ^{235}U nucleus) are absorbed by nuclei causing further fission and so producing more neutrons. The energy released can be estimated by using the Einstein's equation:

$$E = mc^2 \quad (11.5)$$

In the fission of $^{235}_{92}U$ by slow neutrons, the mass of reacting particles is equal to the sum of the isotopic mass of $^{235}_{92}U$, i.e., 235.118 m_u, and the mass of one neutron, i.e., 1.009 m_u making up a total of 236.127 m_u. We have seen that uranium nucleus splits in different ways; in one of such fission products, the sum of the isotopic masses with two neutrons is 94.936 (for $^{95}_{42}Mo$) + 138.95 (for $^{139}_{57}La$) + 2 × 1.009 (for two neutrons) = 235.904m_u. Hence, the mass converted into energy is

= (236.127 – 235.904) m_u

= 0.223 m_u

Since 1 m_u = 931.48 MeV, for one ^{235}U fission, the energy released = 0.223 × 931.48~ 208 MeV, which corresponds to about 8.4 × 10^7 kJ of energy per gram of $^{235}_{92}U$.

The key to the liberation of energy in the nuclear fission reaction is the production of two or more neutrons per reaction initiated by one neutron. Since each of these neutrons can initiate a further nuclear reaction, a branching **chain reaction** is possible and if this takes place in a quantity of $^{235}_{92}U$ larger than a certain critical amount (so that only a few neutrons escape), a violent explosion with enormous liberation of energy ensues. This is the principle underlying the fission type of nuclear or atom bomb. Schematic view of fission chain reaction is presented in Fig.11.6.

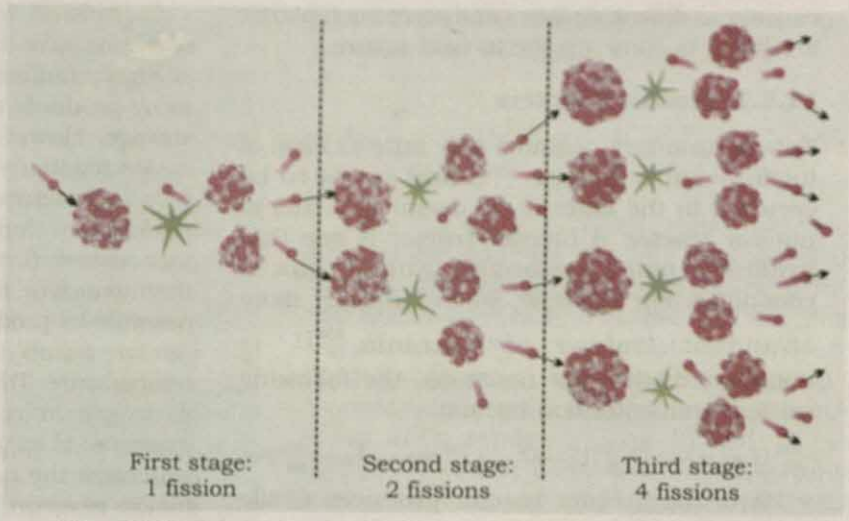


Fig. 11.6 *Schematic view of the start of a fission chain reaction.*

11.5.1 Nuclear Reactors

If the nuclear fission reaction is made to occur at a controlled rate, the energy released can be harnessed for peaceful rather than destructive purposes. The equipment employed to carry out controlled fission reactions is called a *nuclear reactor* (Fig. 11.7). A nuclear reactor consists of three components:

(a) a fissile material (uranium enriched in $^{235}_{92}U$, say, 2-3%),

(b) a moderator (graphite or heavy water, D_2O) to slow down the neutrons so that they are captured and become effective to bring about fission reaction, and

(c) control rods made of boron steel or cadmium, which are capable of absorbing neutrons and are used to ensure that the neutron flux is under control. The control rods are inserted into the reactor and can be raised or lowered to control the chain reaction.

The large amount of energy released from the fission is used for steam generation through heat exchangers to produce electricity. Twelve such nuclear power plants have been set up in our

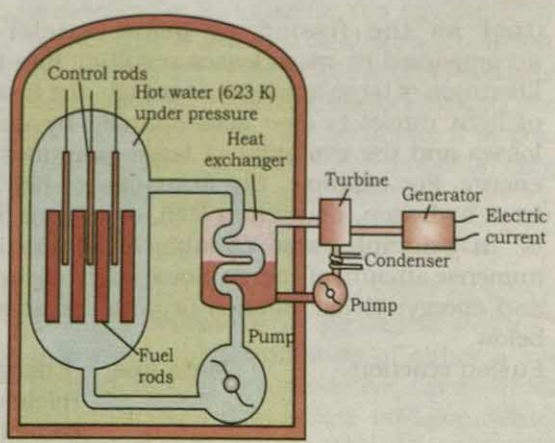


Fig. 11.7 *A Schematic diagram of one type of nuclear reactor. This one is pressurized water reactor, in which coolant is water under pressure.*

country at different places and more such plants are likely to come up the in near future.

11.5.2 Breeder Reactors

Natural uranium contains very little (0.72%) of its fissionable isotope ^{235}U and needs to be enriched in the latter to be useful as a fuel in nuclear reactor. A breeder reactor is one that produces more fissionable nuclei than it consumes. For example, when naturally more abundant isotope of uranium, $^{238}_{92}U$ is bombarded with fast neutrons, the following nuclear transmutation occurs:

$$^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{92}U \xrightarrow{-\beta^-} ^{239}_{93}Np \xrightarrow{-\beta^-} ^{239}_{94}Pu$$

Here, the breeder reactor produces fissile $^{239}_{94}Pu$ from non-fissile uranium. Similarly, naturally more abundant isotope of thorium, $^{232}_{90}Th$, can be used to produce a fissible or fissionable isotope of uranium, $^{233}_{92}U$. Thus,

$$^{232}_{90}Th + ^{1}_{0}n \longrightarrow ^{233}_{90}Th \xrightarrow{-\beta^-} ^{233}_{91}Pa \xrightarrow{-\beta^-} ^{233}_{92}U$$

In all reactors, heat from the core is extracted by heat exchangers and is used to convert water into steam, this is then used to drive turbo-alternators for producing electricity. In breeder reactors, an alloy of sodium and potassium is used as coolant. The liquid metal gives its heat to water in a heat-exchanger.

11.6 NUCLEAR FUSION

Just as the fission of heavy nuclei is accompanied by mass losses resulting into the liberation of large amounts of energy, the fusion of light nuclei is also accompanied by mass losses and the evolution of large quantities of energy. For example, the formation of helium from hydrogen, deuterium ($^{2}_{1}H$), or tritium ($^{3}_{1}H$) is, in principle, also capable of generating immense amount of energy. Some such reactions and energy release in each process are shown below,

Fusion reaction	Mass loss	Energy released (kJ mol^{-1})
$^{2}_{1}H + ^{2}_{1}H \longrightarrow ^{4}_{2}He$	0.026	2.3×10^9
$^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n$	0.018	1.79×10^9
$4\,^{1}_{1}H \longrightarrow ^{4}_{2}He + 2\beta^+$	0.029	2.6×10^9

Compared with fission reactions, fusion reactions have the advantage that large amounts of highly radioactive nuclides are not obtained as by-products which may pose problem of safe storage. However, the activation energies for fusion reactions are very high, i.e., they require very high temperature (> 10^6 K) to overcome electrostatic repulsion between the nuclei. For this reason, fusion reactions are referred to as *thermonuclear reactions*. Till date, it has been possible to produce a fusion reaction only if a fission bomb is used to generate the high temperature. This is the principle underlying the hydrogen or thermonuclear bomb. A fusion explosion is triggered by an atomic bomb which generates the high temperature needed for the fusion reaction.

Fusion reactions are believed to take place in the sun and stars at temperatures above 10^7K, and the following processes have been suggested as the chief source of sun's energy:

$$^{1}_{1}H + ^{1}_{1}H \longrightarrow ^{2}_{1}H + \beta^+ + \text{neutrino}$$

$$^{1}_{1}H + ^{2}_{1}H \longrightarrow ^{3}_{2}He + \gamma 3$$

$$^{3}_{2}He + ^{3}_{2}He \longrightarrow ^{4}_{2}He + 2\,^{1}_{1}H$$

or in sum,

$$4\,^{1}_{1}H \longrightarrow ^{4}_{2}He + 2\beta^+ + 2\,\text{neutrino}$$

Intensive research is now under way to produce controlled fusion reactions by lasers in a plasma (an ionized gas at high temperature) but so far no success has been reported in this regard.

Example 11.9

Calculate the energy released per atom of helium in the following:

$$^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n$$

(Given the masses : $^2H = 2.014$; $^3H = 3.016$; $He = 4.003$; $n = 1.009\ m_u$)

Solution

Mass on the reactant side
$= 2.014 + 3.016 = 5.030\ m_u$

Mass on the product side
$= 4.003 + 1.009 = 5.012\ m_u$

Mass loss $= 5.030 - 5.012 = 0.018\ m_u$

Energy released per atom of helium
$= (0.018 \times 931)$ MeV $= 16.76$ MeV

Nuclear Waste Disposal A Big Problem

The used up uranium fuel rods from nuclear power plants, are among the deadliest substances known to man. Nuclear power plants use the nuclear energy produced in nuclear fission to heat water which turns turbines that generate electricity. Each rod is 14-18 feet metal tube filled with uranium pellets.

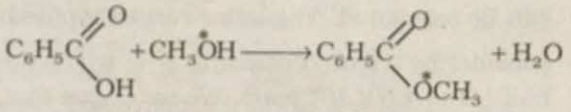
While a rod powers the plants for 18 months, it is dangerous for 10,000 years. It can eat flesh and cause cancer and birth defects. Nuclear power plants have been storing old fuel rods in big swimming pools like concrete tanks. However this practice cannot continue, say the people who run the power plants. In years to come, the power plants may be running out of space to store it. And as it piles up, there is a greater chance the 'hot' water could leak through the ground and to the water under the earth's surface.On a smaller scale, nuclear waste is disposed off by dumping it in thick lead (Pb) containers which are buried in the earth by drilling holes. However, the disposal of nuclear waste is a big problem before the countries which depend on nuclear power plants for their electricity resources in a big way. There are over four hundred power plants globally which generate about 17 percent of world's electricity. In USA alone there are 131 power plants which generate 20 percent of the country's electricity; there by producing 2000 tonne of nuclear waste each year. Its disposal is indeed a big problem.

11.7 APPLICATIONS OF RADIOACTIVITY AND RADIOISOTOPES

Radioisotopes find numerous uses in different areas such as medicine, chemistry, biology, archeology, agriculture, industry, and engineering. In this section, we shall present some important applications of radioisotopes.

11.7.1 Tracers

By incorporating a small amount of a radioisotope in a reaction system, one can trace the course of the reaction. Such a sample of radioisotope is called *tracer*. Since all the isotopes of an element are chemically equivalent, the monitored path of the isotope will indicate the path of the reaction. For example, consider the problem of determining the course of an esterification such as:



Does the starred oxygen come from alcohol or from the acid? By labelling the oxygen atom of methanol with ^{18}O and then using it in the esterification, it can be proved that the starred oxygen comes from the alcohol and not from the acid as the ester is found enriched with ^{18}O isotope. Many other mechanistic applications have been reported. The use of ^{14}C as a radioactive tracer using labelled compounds is well known. The dynamic nature of chemical equilibria has been established by the use of labelled compounds.

11.7.2 Activation Analysis

The absorption of neutron by any nucleus produces an 'activated' or energy rich species that decays by a process characteristic of the nucleus involved. The various isotopes of elements differ considerably in their ability to absorb neutron. By irradiating a mixture of nuclei with neutrons to saturation limit, it is possible to selectively activate certain elements, detect their presence and measure their concentration by measuring the intensity of the induced radioactivity. The sensitivity of the neutron activation analysis depends on the neutron flux available for irradiation, the availability of nucleus to absorb a neutron and the energy of the decay process. This method is very useful for determination of elements present in trace quantities. For example, it is possible to detect as little as 10^{-40}g of copper or tungsten by activation analysis.

11.7.3 Age of Minerals and Rocks

The determination of age of minerals and rocks is an important part of geological studies. This may involve determination of either a species formed during a radioactive decay or of the residual activity of an isotope which is undergoing decay.

The former may be illustrated by helium dating. Helium present in uranium mineral has almost certainly been formed from α-particles. A gram of uranium in equilibrium with its decay

products produces approximately 10^{-7}g of helium per year. So if the helium and uranium contents of a mineral are known, the age of the mineral can be estimated. The latter can be typified by considering a rock containing $^{238}_{92}U$ which has a half-life of 4.5×10^9 years. We have seen that in the uranium decay series, $^{238}_{92}U$ after a series of decay gives the stable isotope $^{206}_{82}Pb$ as the end product. Assuming that initially the rock did not contain any lead, we can determine the age of the rock by measuring the ratio of $^{238}_{92}U$ and $^{206}_{82}Pb$ and using the equation,

$$N_t = N_o e^{-kt}$$

where N_o and N_t are the amounts of uranium present initially ($t = 0$) and after the lapse of time t, respectively and k is the decay constant. Suppose, the molar ratio of uranium and lead is 1:1, it means half of the uranium originally present has undergone decay, finally giving the lead isotope. The age of the rock in that case will be equal to the half-life period of $^{238}_{92}U$ (i.e., 4.5×10^9 years). Most of the rocks contain lead/uranium ratio much less than unity indicating that the age of rocks may be less than the half-life period of $^{238}_{92}U$.

11.7.4 Radiocarbon Dating

Radiocarbon ($^{14}_{6}C$) dating of historical wooden-derived objects is based on the knowledge that the cosmic ray intensity (responsible for ^{14}C production) has been practically constant for thousands of years. ^{14}C is formed in the upper atmosphere by the action of cosmic radiation on ^{14}N,

$$^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{14}_{6}C + {}^{1}_{1}H$$

The ^{14}C so produced is eventually converted into carbon dioxide, which in turn is incorporated into plants and trees by the process of photosynthesis and then finds way into animals which eat plants. Because of the natural plant-animal cycle, an equilibrium is set up and all living matter contains the same small proportion of ^{14}C as it occurs in the atmosphere. Once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ^{14}C in the dead begins to fall due to the decay which ^{14}C undergoes.

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + \beta^-$$

The half-life ($t_{1/2}$) period of ^{14}C is 5770 years. A comparison of the β^- activity of the dead matter with that of the carbon still in circulation enables measurement of the period of isolation of the material from the living cycle. The method, however, ceases to be accurate over periods longer than two or three half-life periods of ^{14}C. The proportion of ^{14}C to ^{12}C in living matter is $1:10^{12}$.

Example 11.10

The beta activity of 1g of carbon made from green wood is 15.3 counts per minute. If the activity of 1g of carbon derived from the wood of an Egyptian mummy case is 9.4 counts per minute under the same conditions, how old is the wood of the mummy case? ($t_{1/2}$ for ^{14}C = 5770 years).

Solution

$k = 0.693 / t_{1/2} = 0.693 / 5770$
$= 1.20 \times 10^{-4}$ year^{-1}
$\log N_o / N_t = kt / 2.303$
$1.20 \times 10^{-4} \times t / 2.303 = \log N_o / N_t$
$= \log 15.3/9.4$
Hence $t = 2.303 / 1.20 \times 10^{-4} \log 15.3 / 9.4$
$= 3920$ years

11.7.5 Uses in Medicines and other Areas

A number of radioisotopes are used in medicine either for diagnosis or treatment. For example, $^{32}_{15}P$ is used for relief in leukemia, $^{131}_{53}I$ is used in the treatment of goiter and cancer and $^{60}_{27}Co$ is used in the treatment of tumours and cancers. The use of radium in the treatment of cancer is well known. Among the industrial applications of radioisotopes are the measurement of bulk flow, mixing efficiency and leak measurements.

SUMMARY

Some naturally occurring elements are found to emit radiation. These elements are said to be radioactive and the phenomenon is known as *radioactivity*. Three types of radiations are emitted from radioactive elements. These are called *alpha*, *beta*, and *gamma* rays. The alpha (α) rays are helium nuclei, beta (β^-) rays are electrons of nuclear origin and gamma (γ) rays are electromagnetic radiation. An alpha emission reduces the atomic number by 2 and the mass number by 4, and a β^- emission advances the atomic number by one unit without changing the mass number. The emission of γ-rays affects neither the mass nor the atomic number.

There are three natural decay series in which heavy nuclei decay by a series of α-and/or β^-- emissions finally resulting in the formation of stable isotopes of lead. The three series start with ^{232}Th, ^{238}U, and ^{235}U and end in ^{208}Pb, ^{206}Pb, and ^{207}Pb, respectively. The fourth is artificial series starting with ^{237}Np and ending in ^{209}Bi. The four decay series are distinguished by whether the mass numbers are exactly divisible by 4 or whether, when divided by four, there are remainders of 1, 2, or 3. For a particular radioactive decay process, the number of nuclei decaying in a short period of time is proportional to the number present and is independent of physical and chemical conditions surrounding the atom. These decay processes follow the first order kinetics. The time taken to reduce the number of nuclei to one-half of the original is referred to the half-life period of a nuclide. The half-life of an unstable isotope is one of its fixed characteristic properties.

Nuclear changes can also be brought about by bombardment of nuclei with accelerated particles like neutrons, deuterons, and protons. There is no essential difference between natural radioactivity and the nuclear changes resulting from such bombardment. All these changes involve the conservation of atomic number and mass number. A particularly important process for the production of artificial radioactive isotope is the (n, γ) reaction which is applied to synthesise new elements. Many of the heavy nuclei can be induced to break up into two fragments of intermediate size and a few neutrons; the process is called *nuclear fission*. In a fission reaction, a loss in mass occurs releasing a vast amount of energy. For the controlled production of energy by nuclear fission, different types of reactors are employed and thus the energy can be put to peaceful uses.

Just as the fission of heavy nuclei is accompanied by large energy release, the fusion of light nuclei is accompanied by mass losses and hence the evolution of large quantities of energy. However, extremely high temperatures are required to initiate fusion reactions. That is why the fusion reactions are also known as *thermonuclear* reactions.

Radioisotopes find a number of applications in different areas. Some of the important ones include their uses as tracers, analytical applications, dating applications and applications in the field of medicines.

EXERCISES

11.1 Clearly state, what do you understand by the terms: mass number, nucleons and nuclides.

11.2 Describe the properties of radiations which are emitted by radioactive nuclei.

11.3 Give one example each of (i) α-emission (ii) β^-- emission and (iii) *K*-capture. Write the equation for these nuclear changes.

11.4 What is the Group Displacement Law? An element belonging to Group 1decays by β^-- emission. To which group of the Periodic table the daughter element will belong?

11.5 How many α- and β^-- particles will be emitted when $^{232}_{90}$Th changes into $^{208}_{82}$Pb?

11.6 Write the nuclear reactions for the following radioactive decay:

(a) $^{238}_{92}U$ undergoes α-decay

(b) $^{234}_{91}Pa$ undergoes β^- - decay

(c) $^{22}_{11}Na$ undergoes β^+ - decay.

11.7 How are the radioactive decay series distinguished? Which one of the decay series is not natural but artificial?

11.8 What kinds of elementary particles are employed for the artificial transmutation of elements? Comment on their effectiveness.

11.9 What is meant by nuclear binding energy? Calculate the binding energy per nucleon of Li isotope, which has the isotopic mass of 7.016 m_u. The individual masses of neutron and proton are 1.008665 m_u and 1.007277m_u, respectively and the mass of electron = 0.000548 m_u.

11.10 The atomic mass of ^{16}O is 15.995 mu while the individual masses of proton and neutron are 1.0073 and 1.0087m_u. The mass of electron = 0.000548 m_u. Calculate the binding energy of the oxygen nucleus in Joules.

11.11 The isotopic composition of rubidium is ^{85}Rb - 72 percent and ^{87}Rb - 28 percent. ^{87}Rb is weakly radioactive and decay by β^-- emission with a decay constant of 1.1×10^{-11} per year. A sample of the mineral pollucite was found to contain 450 mg Rb and 0.72 mg of ^{87}Sr. Estimate the age of mineral pollucite, stating any assumption made.

11.12 The isotopic masses of $^{2}_{1}H$ and $^{4}_{2}He$ are 2.0141 and 4.0026 m_u respectively and the velocity of light in vacuum is 2.998×10^8 ms^{-1}. Calculate the quantity of energy (in J) liberated when two moles of $^{2}_{1}H$ undergo fusion to form one mole of $^{4}_{2}He$.

11.13 The radioactive isotope $^{60}_{27}Co$ which has now replaced radium in the treatment of cancer can be made by a (n, p) or (n, γ) reaction. For each reaction, indicate the appropriate target nucleus. If the half-life of $^{60}_{27}Co$ is 7 years, evaluate the decay constant in s^{-1}.

11.14 A piece of wood from an archeological source shows a ^{14}C activity which is 60% of the activity found in fresh wood today. Calculate the age of the archeological sample. ($t_{1/2}$ ^{14}C = 5770 years)

11.15 What is a nuclear fission reaction? Explain the principle of atomic bomb and working of a nuclear reactor to produce electricity.

11.16 What is meant by fissionable or a fissile isotope? How are such isotopes produced artificially? Give an example.

11.17 In the neutron-induced fission reaction of $^{235}_{92}U$, one of the products is $^{95}_{37}Rb$, in this mode, another nuclide and three neutrons are also produced. Identify the other nuclide.

11.18 Explain the principle of:

(a) Activation analysis (b) Breeder reactor.

11.19 Describe the chief applications of radioisotopes in:

(a) The study of reaction mechanism (b) Medicines.

11.20 Complete the following nuclear reactions:

(a) $^{96}_{42}Mo$ (.....,n) $^{97}_{43}Tc$ (b) ..... (α, 2n) $^{211}_{85}At$

(c) $^{55}_{25}Mn$ (n,γ) ... (d) $^{246}_{96}Cm + {}^{12}_{6}C \longrightarrow$ ..... + $4\,{}^{1}_{0}n$

(e) $^{27}_{13}Al$ (α,n) .... (f) $^{238}_{92}U$ (α, β^-) .....

11.21 Complete the equations for the following nuclear processes:

(a) $^{35}_{17}Cl + {}^{1}_{0}n \longrightarrow$ ..... + $^{4}_{2}He$

(b) $^{235}_{92}U + {}^{1}_{0}n \longrightarrow \ldots\ldots + {}^{137}_{54}Xe + 2\,{}^{1}_{0}n$

(c) $^{27}_{13}Al + {}^{4}_{2}He \longrightarrow \ldots\ldots + {}^{1}_{0}n$

(d) $\ldots\ldots (n,p)\ {}^{35}_{16}S$

(e) $^{239}_{94}Pu\ (\alpha, \beta^-)\ \ldots\ldots$

11.22 Calculate the mass of ^{140}La in a sample whose activity is 3.7×10^{10} Bq (1 Becquerel, Bq = 1 disintegration per second) given that its $t_{1/2}$ is 40 hours.
[Hint: Mass = $3.7 \times 10^{10} \times 40 \times 60 \times 60 \times 140/(N_A + \ln 2)$].

11.23 Calculate the binding energy per nucleon for ^{12}C, ^{14}N, ^{16}O, and comment on their relative magnitudes. Masses of proton and neutron are 1.0078 and $1.0087m_u$ respectively. ($1m_u$ = 931 MeV)

11.24 The β^- activity of a sample of CO_2 prepared from a contemporary wood gave a count rate of 25.5 counts per minute (c.p.m). The same mass of CO_2 from an ancient wooden statue gave a count rate of 20.5 c.p.m in the same counter condition. Calculate its age to the nearest 50 years taking $t_{1/2}$ for ^{14}C as 5770 years. What would be the expected count rate of an identical mass of CO_2 from a sample which is 4000 years old?

11.25 How is ^{14}C produced in nature and what happens to it subsequently? Give equations for these processes.

11.26 What do you understand by *tracers*? Give an example of a tracer that can be used in determining the mechanism of a chemical reaction.

11.27 What are synthetic elements? Mention two synthetic elements and write the nuclear equations leading to their synthesis.

11.28 What is meant by thermonuclear reactions and why are they so called? Why are these reactions not useful for peaceful purposes?

11.29 Describe the principle of an atom bomb. What is meant by a critical mass? What is the critical mass of $^{235}_{92}U$?

UNIT 12

STEREOCHEMISTRY

OBJECTIVES

After studying this Unit, you will be able to:

- understand some basic stereochemical principles, terms and notations.
- learn about optical activity, and molecular asymmetry.
- understand the meaning of enantiomers, diastereoisomers and *meso* compounds.
- learn about racemisation and resolution.
- appreciate the importance of chirality in chemical and biological processes.

"Molecular asymmetry is one of the mechanisms of life."

The concept of isomerism in organic compounds has already been introduced in class XI. Different structural arrangements of a molecule constituted from the same atoms are referred to as *isomers* (a term used by Berzelius in 1830, is derived from Greek words *isos* meaning equal and *meros* meaning parts). *Stereoisomers are the molecules that have the same atomic connectivities but different disposition of atoms or groups in space.* Thus, in stereoisomers, atoms are connected to each other in the same way, but they differ from each other with respect to their relative orientation in three-dimensional space. *Stereochemistry* is the study of spatial arrangements of atoms in molecules, i.e., how various atoms or groups of atoms in a molecule are arranged relative to one another in three-dimensional space.

Stereoisomers are of two types: *conformational* and *configurational isomers.* Conformational isomers (Class XI, Unit 15) differ from each other with respect to the relative positions of some of the atoms in the molecule in three-dimensional space due to rotation about sigma bonds. The interconversion of these isomers does not require breaking and re-making of covalent bonds. Configurational stereoisomers on the other hand are due to certain types of rigidity within the molecule, and these isomers can be interconverted only by breaking and re-making of covalent bonds and not simply by rotation about sigma bonds.

There are two types of configurational isomers: *geometrical* and *optical.* You are already familiar with geometrical isomers (the *cis-trans* or *E-Z* isomers), and in this Unit, you will learn about optical isomerism.

12.1 PLANE-POLARISED LIGHT AND OPTICAL ACTIVITY

You may be aware that ordinary light can be considered as an electromagnetic wave, which has oscillations in all the directions perpendicular to the path of propagation. Under certain conditions, light can be made to have all its oscillations in the same plane and is called *plane-polarised light*. The plane-polarised light can be produced by passing ordinary light through a *Nicol prism*. A Nicol prism is made from calcite, a special crystalline form of calcium carbonate.

Certain compounds rotate the plane of polarised light in a characteristic way when it is passed through their solutions. These compounds are referred to as *optically active* compounds. The angle of rotation by which the plane-polarised light is rotated, can be measured by using an instrument called *polarimeter*. A schematic diagram of a polarimeter is shown in (Fig. 12.1). Unpolarised light emitted by a sodium lamp (the sodium D line 589.3 nm) passes through a polariser. This plane-polarised light on passing through the polarimeter tube containing an optically active sample emerges with its plane of polarisation rotated from its original position. A second Nicol prism called analyser is placed in the path of light coming out of the sample, can be rotated by certain angle to compensate for the rotation of the plane of the plane-polarised light by the optically active sample. If the substance rotates plane-polarised light to the right, i.e., in clockwise direction, it is called *dextrorotatory* (Greek for right rotating) or the *d*-form and it is indicated by placing a positive (+) sign before the degrees of rotation. If light is rotated towards left, i.e., in anti-clockwise direction, the substance is said to be *laevorotatory* (*Greek* for left rotating) or the *l*-form and a negative (–) sign is placed before the degrees of rotation. Currently, dextro and laevo rotations are represented by algebraic signs of (+) for dextro and (-) for laevo (instead of *d* and *l*).

The extent of experimentally observed angle of rotation (*optical rotation*, symbolised as α_{obs}) of a substance depends on the wavelength of the light and the number of optically active molecules in the path of the light beam (which depends on the concentration of the sample and the length of the sample tube). Other factors that influence α_{obs} are the solvent used and the temperature at which the measurement is made. The optical rotation of an optically active compound is expressed in terms of *specific rotation*, $[\alpha]$.

$$[\alpha] = \frac{\text{Observed rotation } (\alpha_{obs})}{\text{Length of tube(dm)} \times \text{concentration of solution} (g\,mL^{-1})}$$

While reporting $[\alpha]$, the wavelength of light used is given as a subscript and the temperature (in degrees celsius) as a superscript. It is also customary to designate the solvent and concentration. Thus, $[\alpha]_D^{25} = -2.25°$ (c. 0.50 ethanol) means that α was measured at 25°C using sodium D line and the sample concentration was 0.50 g/mL in ethanol.

12.2 MOLECULAR ASYMMETRY, CHIRALITY AND ENANTIOMERS

The foundation for modern stereochemistry was laid when Louis Pasteur in 1848 observed that crystals with mirror images of each other exist. He demonstrated that the aqueous solutions of both types of the crystals showed optical rotation, that was equal in magnitude (for solutions of equal concentration) but opposite in direction. Pasteur believed that this difference in optical activity was associated with the three-dimensional arrangement of atoms in the two

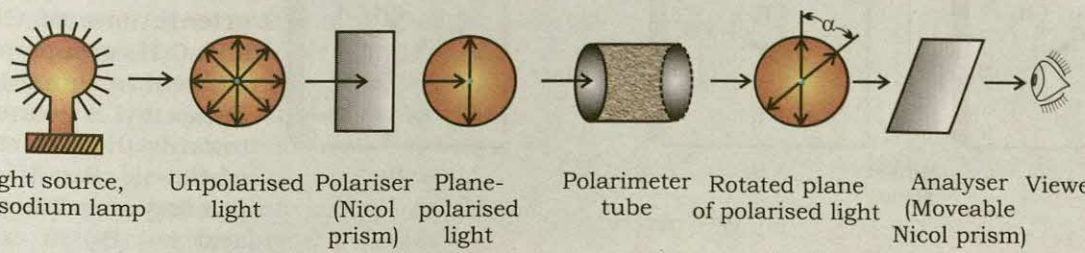


Fig. 12.1 *Schematic representation of a polarimeter showing measurement of optical activity.*

types of crystals. In 1874, J. van't Hoff and C. Le Bel independently, proposed that all the four valencies of carbon are directed towards the four corners of a regular tetrahedron, and if all the four substituents attached to such a carbon are different, the resulting molecule would lack symmetry. Such a molecule is referred to as *asymmetric molecule* and asymmetry of the molecule is responsible for optical activity in such organic compounds.

The symmetry and asymmetry are also observed in many day-to-day objects. A sphere, a cube, a cone and a tetrahedron are all identical to their mirror images, and can thus be superimposed. Such objects whose projections are superimposable on their mirror images are **symmetrical objects**. Many objects are, however, non-superimposable on their mirror images. For example, your left hand looks similar to the right hand. But if you put your left hand on your right hand (Fig. 12.2), these do not coincide. They are non-superimposable mirror images of one another. The general property of handedness is called chirality. **Objects** which are non-superimposable on their mirror images are said to be **chiral,** while the objects which are superimposable on their mirror images are **achiral**.

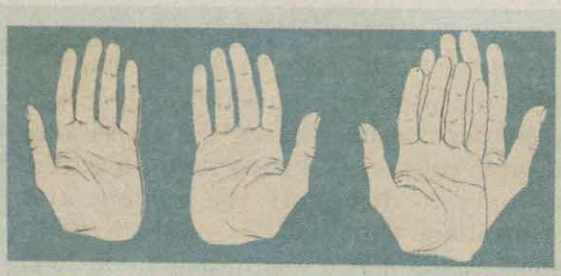


Fig. 12.2 *Non-superimposable right and left hands.*

Now, let us extend the concept of non-superimposability to organic molecules. Let us consider two simple molecules, 2 chloropropane and 2-chlorobutane and examine them by overlap procedure whether they are chiral or achiral.

The two mirror image forms of 2-chloropropane are A and A_1 [Fig. 12.3(a)]. Let us reorient A_1 to see if it can be superimposed on A. We do it by mentally picking up A_1, rotating it by 180º so that C–Cl bonds in the two images project in the same direction. A_2 is obtained by so rotating A_1. Now, mentally place A_2 over A. You will find that A and A_2 are superimposable. Hence, 2-chloropropane is **achiral**.

Now, let us consider 2-chlorobutane. It contains a carbon attached to a H, Cl, CH_3 and C_2H_5. The mirror image of B is B_1 [Fig. 12.3(b)]. Let us reorient B_1 to get B_2 and find whether it can be superimposed on B. You will notice that B and B_2 do not match. The central carbon, the H and Cl atoms can be superimposed but the spatial orientations of CH_3 and C_2H_5 groups are different in B and B_2. In B, ethyl is pointing towards the observer while in B_2, it is pointing away. Thus, B and B_2 are non-superimposable and 2-chlorobutane

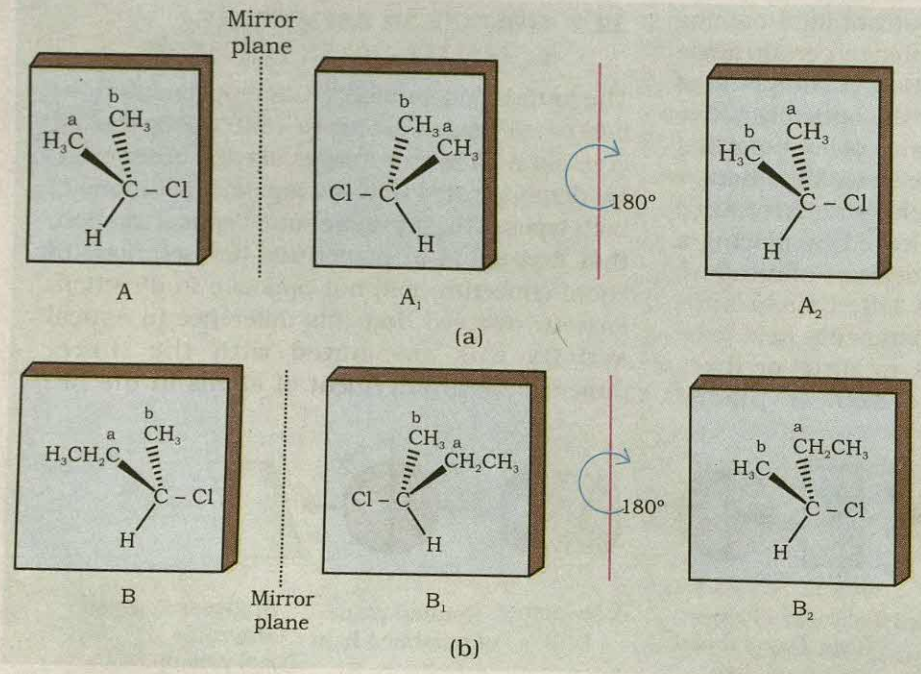


Fig. 12.3 *(a) Projections of 2-chloropropane and (b) 2-chlorobutane.*

is a chiral molecule. The most common indicator of chirality is the presence of a carbon bonded to four different substituents. The molecule C_{ABCD} where A, B, C and D are the four different substituents covalently linked to carbon is an asymmetric molecule e.g. lactic acid (Fig. 12.4). If we draw a three dimensional wedge and dash formula for this molecule and hold it in front of a mirror, we will get mirror image of the molecule as illustrated in Fig. 12.4. These two molecules are stereoisomers.

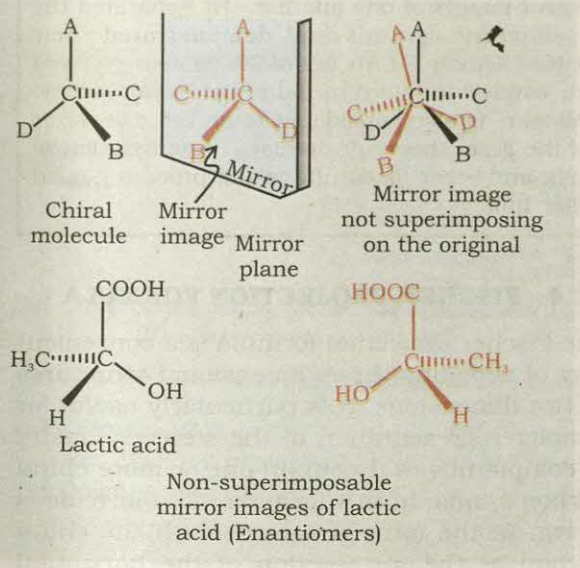


Fig. 12.4 *Non-superimposable mirror images of chiral molecules.*

When a molecule contains one asymmetric carbon, it is always chiral. Common examples of chiral molecules are 2,3-dihydroxypropanal, ($OHC-CHOH-CH_2OH$, glyceraldehyde), 2-hydroxy propanoic acid ($CH_3-CHOH-COOH$, lactic acid), bromochloroiodomethane (BrClCHI) etc. These are asymmetric molecules.

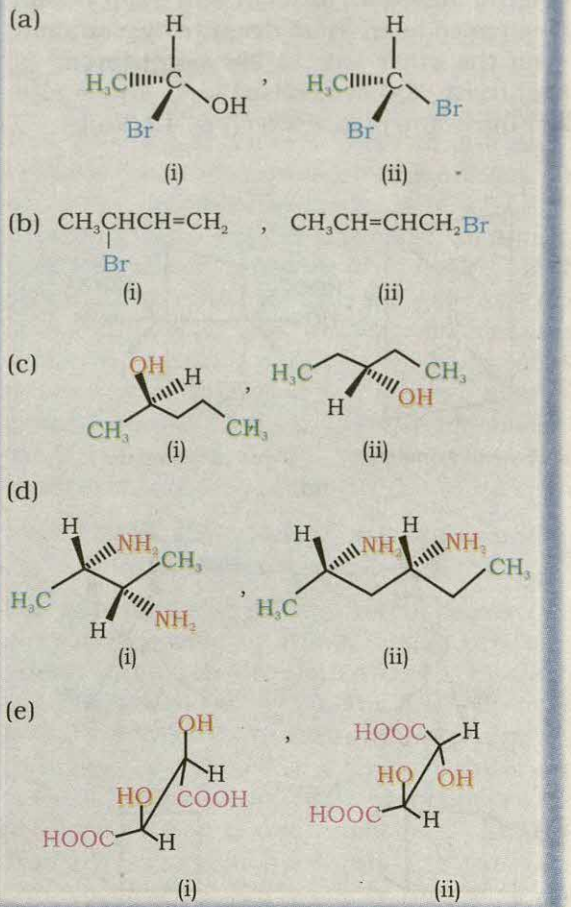
The necessary condition for chirality is not just the presence of asymmetric carbon atoms but the asymmetry of the molecule as a whole.

The stereoisomers related to each other as non-superimposable mirror images are called *enantiomers*. For example, the two structures shown in Fig. 12.4 are enantiomers as they bear non-superimposable mirror image relationship. Enantiomers possess identical physical properties, namely, melting point, boiling point, solubility, refractive index etc. They differ only with respect to the sign of specific rotation. One of the enantiomer will be *dextro*rotatory while the other *laevo*rotatory. A mixture containing the two enantiomers (dextro and laevo) in equal proportions will have zero optical rotation as the rotation due to one enantiomer cancels the rotation due to the other. Such a mixture is known as **racemic mixture** or **racemic modification**.

A racemic mixture is represented by prefixing *dl* or (±) before the name, such as (±) butan-2-ol. The process of conversion of an enantiomer into a racemic mixture is known as **racemisation**.

Example 12.1

Identify **chiral** and **achiral** molecules in each of the following pair of compounds.



Solution

Chiral : a(i), b(i), c(i), d(ii), e(ii)
Achiral : a(ii), b(ii), c(ii), d(i), e(i)

12.3 ELEMENTS OF SYMMETRY

A molecule as a whole is asymmetric if it does not possess any element of symmetry such as (i) plane of symmetry, (ii) centre of symmetry, (iii) axis of symmetry, and (iv) alternating axis of symmetry. The first two kinds of symmetry elements relevant to the discussions in this Unit, are briefly described below.

Plane of symmetry: The plane of symmetry of a molecule represents a plane bisecting the molecule such that each half of the molecule is the mirror image of the other half. The plane of symmetry is called a sigma (σ) plane or a mirror plane [Fig. 12.5(a)].

Centre of symmetry: The centre of symmetry is defined as that point (atom) in a molecule from which if a straight line is drawn from any part of the molecule through that point (atom) and extended to an equal distance by a straight line on the other side, a like point (atom) is encountered. It is symbolised as C_i and is also called the *centre of inversion* [Fig. 12.5(b)].

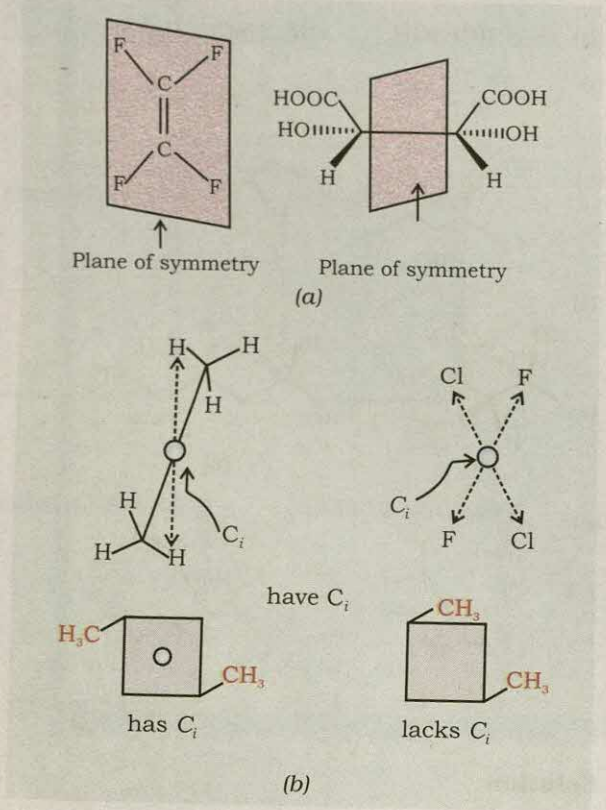


Fig. 12.5 *(a) Plane of symmetry (b) Centre of symmetry (C_i).*

LOUIS PASTEUR
(1822 - 1895)

Louis Pasteur, born on December 27, 1822 in Dole, France started his scientific career in chemistry by studying the shapes of crystals. Pasteur examined the crystals of tartaric acid carefully and noted that while the crystals of pure tartaric acid were of only one type, the paratartaric acid is made of two asymmetric types of crystals, which are mirror images of one another. He separated the asymmetric crystals and demonstrated their optical activity. At the age of 26, Pasteur received the coveted Rumford medal of the Royal Society. Pasteur is also considered to be the discoverer of the germ theory of disease. Pasteurisation of milk and other foodstuffs is the process named after him.

12.4 FISCHER PROJECTION FORMULA

The Fischer projection formula is a convenient way of depicting three-dimensional structures in two-dimensions. It is particularly useful for simpler representation of the stereochemistry of compounds that contain one or more chiral carbon atoms. In this formula, the molecule is drawn in the form of a cross with the chiral carbon at the intersection of the horizontal and vertical lines. The chiral carbon is not explicitly shown by atomic symbol in the Fischer projection. The four groups attached to the chiral carbon are placed on the four ends of the cross. The horizontal lines represent the bonds directed towards the viewer, and the vertical lines away from the viewer. A Fischer projection formula for bromochlorofluoromethane that contains one chiral carbon is shown in Fig. 12.6(a). For molecules containing serveral carbons, it is customary to orient the molecule in such a way so that the carbon chain is vertical, as illustrated by drawing the Fischer projection formula for glyceraldehyde in Fig. 12.6(b) from its 3D wedge-and-dash formula. Although the Fischer projections are planar structures, these can be rotated end-for-end in the plane of the paper only in multiples of 180 degrees, but not 90 degrees at a time. Also, a Fischer projection formula may not be taken out of the plane of the paper and flipped over.

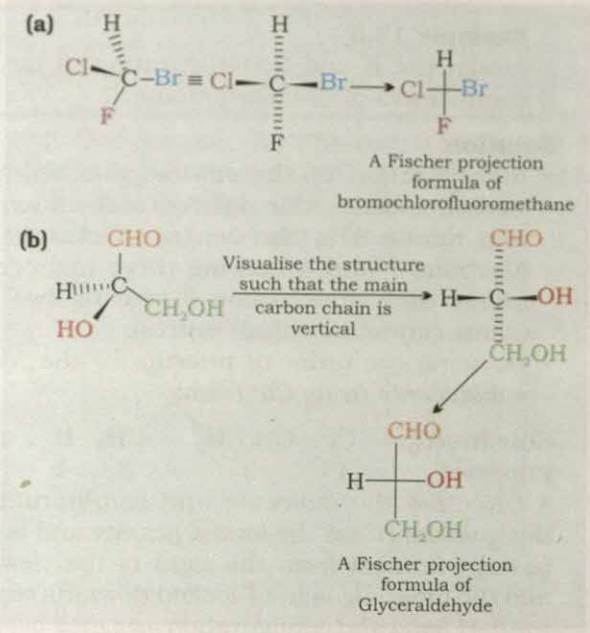
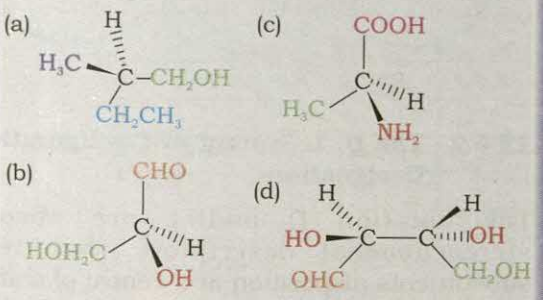


Fig. 12.6 Representing 3D structural molecules using 2D Fischer projection formula.

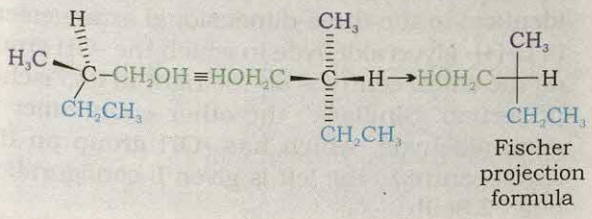
Example 12.2

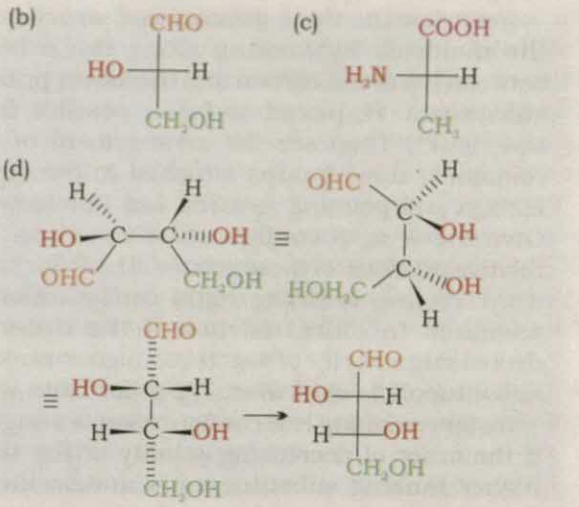
Draw Fischer projection formulas for the following molecules:



Solution

(a) View the structure such that H_3C-C-C_2H_5 is aligned vertically with the -CH_3 and C_2H_5 groups extending away from you. Replace the wedge-and-dash bonds by straight lines to get the Fischer projection formula.





12.5 ABSOLUTE CONFIGURATION: THE *R*, *S* AND D, L CONFIGURATION DESCRIPTORS

The three-dimensional structure of a molecule that has one or more centres of chirality is referred to as its *absolute configuration*. The *absolute stereochemistry* refers to an unambiguous specification of all spatial positions about a centre of chirality. In the preceding sections, we have seen the existence of two stereoisomers for a compound containing a centre of chirality. These configurationally different compounds (enantiomers) must be properly designated for their stereochemical identity. Two such conventions for configurational designation are described below.

12.5.1 The *R*, *S* Convention of Configurational Designation

For specifying absolute stereochemistry, a method (accepted by IUPAC) using prefixes *R* and *S* has been developed by R. S. Cahn, C. K. Ingold and V. Prelog. The first step in the *R*, *S* convention is to identify the centre(s) of chirality. The second step is to assign the priority to each group attached to the chiral centre. The priority (based on atomic number of the attached atom) is assigned by employing the same *Cahn-Ingold-Prelog(CIP)* priority rules employed to describe *E* and *Z* isomers that you learnt in Class XI (Unit 15). Consider, 1-bromo-1-chloroethane as an example. According to CIP priority rule, the order of decreasing priority of substituents is as follows:

$$Br > Cl > CH_3 > H$$

Now view the three dimensional structure of the molecule by looking along the σ bond between the chiral carbon and the lowest priority substituent, H, placed as far as possible from the viewer. Then see the arrangement of the remaining three groups attached to the chiral carbon and pointing towards you (the viewer). Give the *R* or *S* configuration based on the relative priorities of these groups. The *R* (for Latin word 'rectus', meaning right) configuration is assigned to chiral carbon if the order of decreasing priority of the three higher ranking substituents is clockwise. The *S* (for Latin word 'sinister', meaning left) configuration is assigned if the order of decreasing priority of the three higher ranking substituents is anticlockwise. Fig. 12.7 illustrates the procedure.

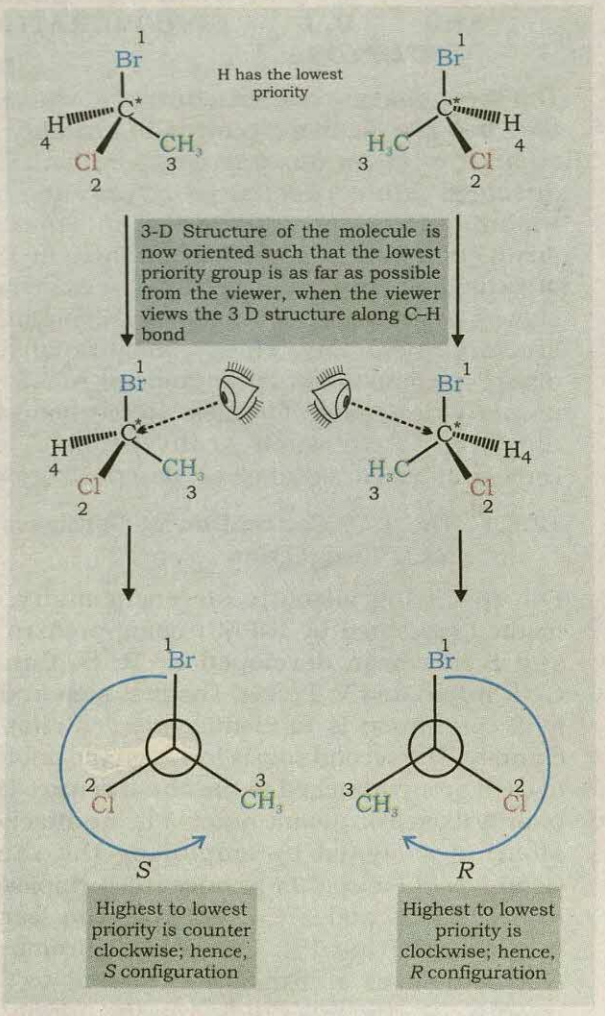


Fig. 12.7 *Designation of R and S configuration employing Cahn-Ingold-Prelog rules.*

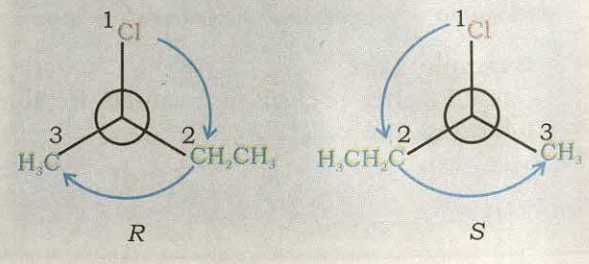
Example 12.3
Assign the *R* and *S* configuration to the enantiomers of 2-chlorobutane.

Solution

- *Identification of the centre of chirality*: Carbon-2 bears four different substituents and hence it is the centre of chirality. (Carbons-1 and 4 bearing three hydrogen atoms each and carbon-3 bearing two H atoms cannot be chiral centres).
- *Deciding the order of priority for the four substituents using CIP rules:*

Substituent:	Cl	$-CH_2CH_3$	$-CH_3$	H
Priority:	1	2	3	4

- *Orienting the molecule and configuration designation*: H has the lowest priority and is to be kept farthest from the sight of the viewer and the molecule is to be looked down through the C-H bond and configuration assigned based on the direction of the remaining three groups is as shown in the following diagram:



12.5.2 The D, L System of Configurational Designation

The notation D and L are absolute stereochemical descriptors that relate substituents disposition at a centre of chirality to that in D- and L-*glyceraldehyde*. (*Relative stereochemistry* gives specification of the stereochemical relation between two molecules). The D- and L-nomenclature to glyceraldehyde (2,3- dihydroxypropanal) was arbitrarily given by Fischer who first introduced this system. The stereochemical designation D refers to an arrangement about a centre of chirality that is identical to the three-dimensional arrangement in D-(+)- glyceraldehyde in which the -OH group on the chiral centre is on the right in its Fischer projection. Similarly, the other enantiomer of glyceraldehyde, which has -OH group on the chiral centre to the left is given L configuration [Fig.12.8(a)].

All molecules, which could be chemically related to D-glyceraldehyde are assigned the D configuration and those related to L-glyceraldehyde are all designated L-configuration as illustrated in fig. 12.8(b). **It may be noted here that there is no direct relation between D,L configurations with *d* and *l* or (+) or (-) notations.**

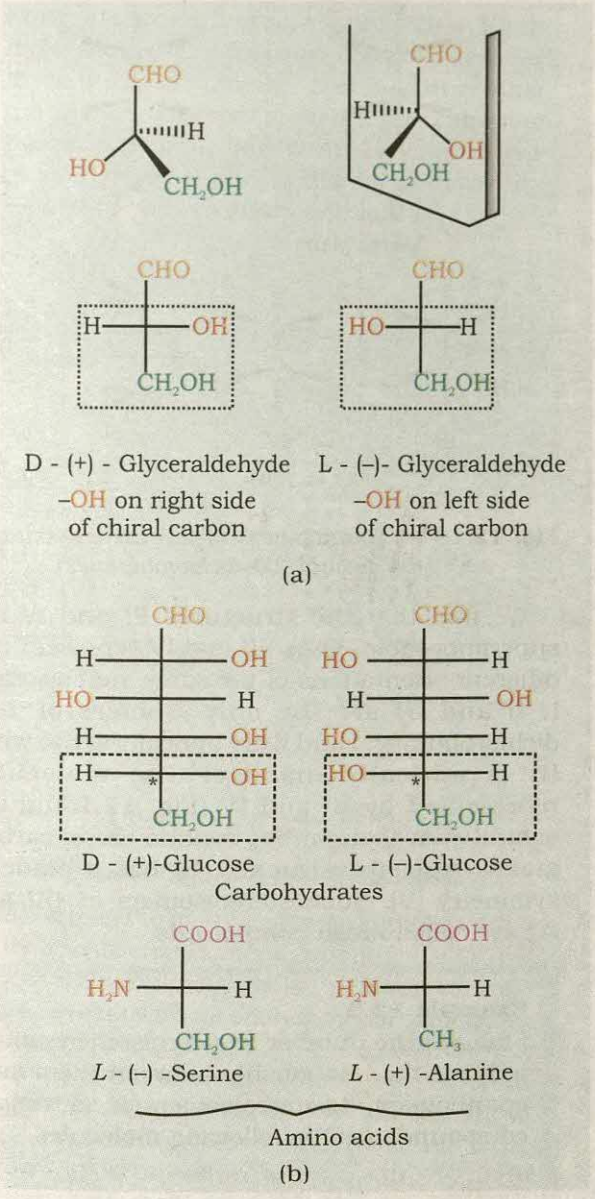
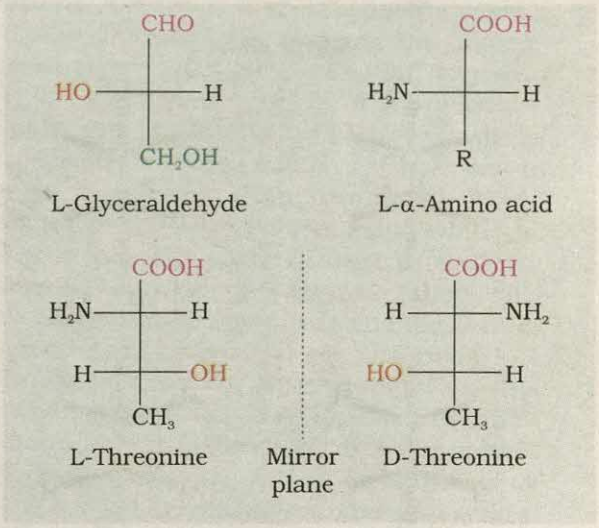
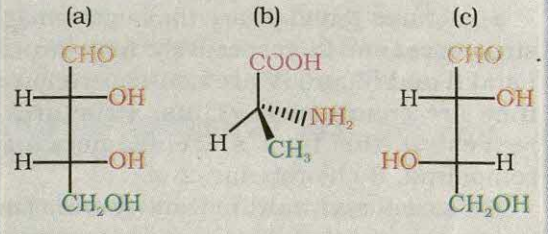


Fig. 12.8 *(a) Three-dimensional and Fischer projections of D-and L-glyceraldehydes.*
(b) Chiral compounds having D and L configuration relative to glyceraldehyde.

In drawing the Fischer projections while assigning D, L configuration, the Fischer projection of the molecule is drawn in such a way that the main longest chain becomes vertical with carbon-1, the most highly oxidized carbon, at the top. The D, L system is commonly used in assigning stereochemistry to carbohydrates and amino acids. For α-amino acids, the configurational arrangement of - NH_2, -COOH, R, and H groups at C_α atom is related to that of the -OH, -CHO, -CH_2OH, and H groups, respectively of glyceraldehyde (2,3–dihydroxypropanal). Thus, (L)-glyceraldehyde, (L)-α-amino acids are said to have the same relative configurations.



Example 12.4
Specify the configuration of the following compounds as D or L.



Solution
D configuration: (a) (-OH on C-3 is on right). L configuration: (b) (convert to Fischer. -NH_2 is on left). (c) (-OH on C-3 is on left side).

12.6 COMPOUNDS CONTAINING MORE THAN ONE CHIRAL CENTRES – DIASTEREOMERS AND *MESO* COMPOUNDS

We have seen that there will be two stereoisomers (i.e. the *R* and *S* enantiomers) for a molecule that contains one centre of chirality. For a molecule containing two chiral centres, we can expect a maximum of four stereoisomers. In general, **for a molecule with *n* chiral centres, there are 2^n possible stereoisomers**. Let us consider 3-chlorobutan-2-ol, which has two centres of chirality.

Now we write the three dimensional structures for all the four ($2^2 = 4$) stereoisomers of this compound (Fig. 12.9).

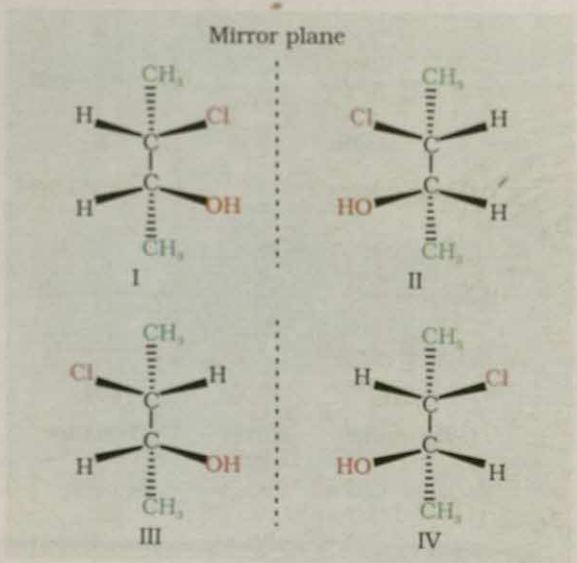


Fig. 12.9 *Four stereoisomers of 3-chlorobutan-2-ol; showing enantiomeric and diastereomeric relationships.*

Structures II and IV are the mirror images of structures I and III, respectively. Also, structures I and II and III and IV are non-superimposable, they are enantiomers. Thus, structures I-IV represent the four stereoisomers of the compound, 3-chlorobutan-2-ol.

The structures I and III or II and IV are not mirror images of each other. These pairs of stereoisomers are **diastereoisomers**. Diastereoisomers have different physical properties.

A compound with two chiral centres does not always have four stereoisomers. Consider 2, 3-dichlorobutane as an example. Now let us write the structural formula of one stereoisomer and its mirror image (Fig. 12.10).

Structures I and II are non-superimposable and thus represent a pair of enantiomers [Fig. 12.10(a)]. Now we write the structure III and its mirror image IV [Fig. 12.10(b)].

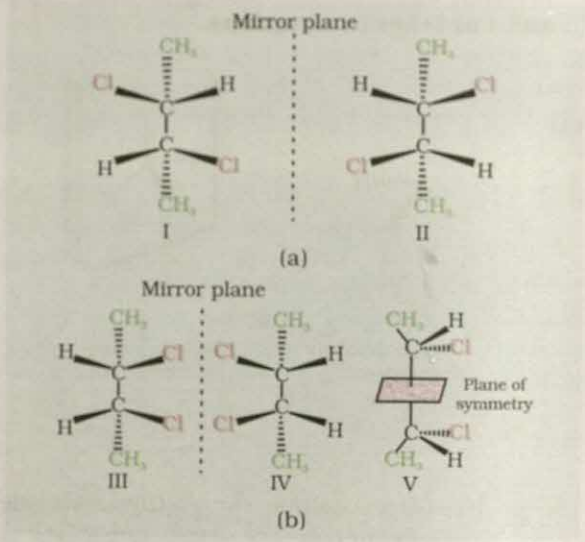
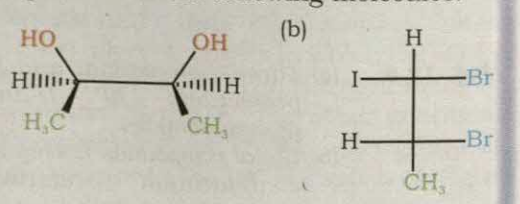


Fig. 12.10 *(a) Enantiomers of 2,3-dichlorobutane. (b) Achiral 2,3-dichlorobutane.*

We find that the structures III and IV are superimposable. Thus, III and IV represent two different orientations of the same stereoisomer. I, II and III are the only isomers of 2,3-dichlorobutane. I and II are optically active while III is optically inactive. The molecules represented by III and IV [Fig. 12.10(b)] are achiral even though they contain chiral carbon atoms. Also, the structure III has a plane of symmetry (V). Such stereoisomers as (III and IV) are called ***meso compounds***.

Example 12.5

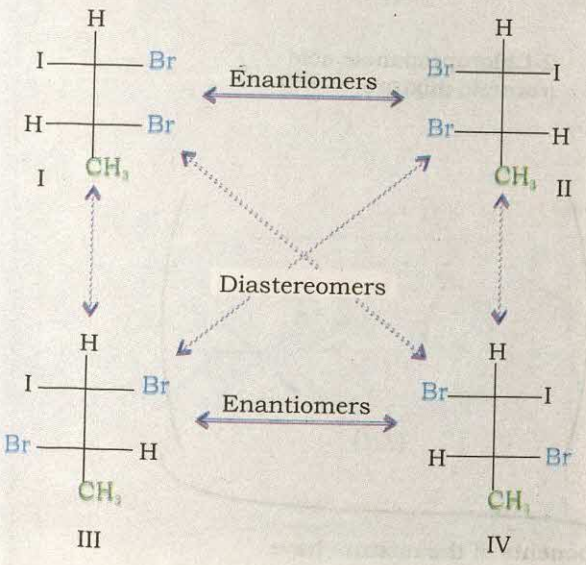
Find out the number of stereoisomers and indicate the relationship between them as enantiomers, diastereoisomers or as *meso* compounds for the following molecules.



Solution

(a) Number of chiral centres = 2. Therefore, maximum number of possible stereoisomers = $2^n = 2^2 = 4$. Molecule also has a mirror plane. Therefore, 3 stereoisomers are possible. One pair of enantiomers and a *meso* form, which is diastereomer of the enantiomers.

(b) Four stereoisomers are possible. Each molecule is the enantiomer of one of the other three (its mirror image) and is at the same time diastereoisomer of each of the remaining two. For example, structure I is enantiomer of compound II and is diastereometrically related to both structures III and IV.



12.7 RESOLUTION OF A RACEMIC MIXTURE

Resolution refers to method of separating a racemic mixture into its enantiomeric constituents. One of the most common methods is to allow a racemic mixture to react with an enantiomer of some other compound. This changes a racemic form into a mixture of diastereomers which have different melting and boiling points, and solubilities. These can be separated from one another by conventional methods of separation of compounds. The separated diastereoisomer is then broken down to give pure enantiomers.

12.8 CHEMICAL REACTIONS AND STEREOCHEMISTRY

Stereochemical considerations are very important in chemical reactivity. When a chemical reaction involves only achiral reactants, solvents and reagents, the products of the reaction are achiral or racemic mixtures. For example, free-radical monochlorination of *n*-butane gives achiral 1-chlorobutane and a racemic mixture of 2-chlorobutane.

$$CH_3CH_2CH_2CH_3 + Cl_2 \xrightarrow{h\nu} CH_3CH_2CH_2Cl + CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$$

Enantiomers show equal reactivity towards achiral reagents, but with chiral reagents their reactivity differs. Reactions of the type in which one of the several possible diastereomeric products predominate are called ***stereoselective reactions***. A reaction is **stereospecific** when a particular stereoisomeric form of the starting material reacts in such a way that it gives a specific stereoisomeric form of the product. Bromine addition to alkenes is an example of stereospecific reaction. Addition of halogens to alkenes produces diastereomers. Thus, (*E*)-alkene gives the *meso* compound while the (*Z*)-alkene gives a racemic mixture. However, if a reaction is carried out using a chiral optically active reagent, only one of the enantiomers or an excess of one enantiomer can be formed. The induction of chirality or asymmetry in this fashion is an interesting feature of such reactions and is referred to as **asymmetric induction**. Asymmetric induction is the use of a chiral reagent or catalyst to convert an achiral reactant to a chiral product having an excess of one of the enantiomers. It is a general principle that optically active products cannot be formed when optically inactive substrates react with optically inactive reagents. Optically inactive starting materials, however, can give optically active products if they are treated with an optically active reagent or if the reaction is catalysed by an optically active substance.

12.9 THE IMPORTANCE OF STEREOCHEMISTRY

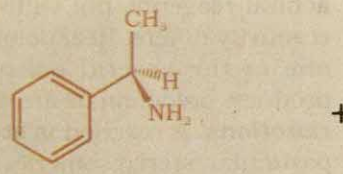
Stereochemistry is an important aspect of carbon compounds. It is prevalent in the whole universe. The human body is structurally chiral with the heart lying to the left and the liver to the right in the body. Many plants show chirality in the way that they wind around supporting structures. Most of the molecules found in plants and animals are chiral and usually only one form

of chiral molecules occurs in a species. All but one of the twenty naturally occurring amino acids that make up proteins have L configuration. The synthesised D-proteins made from D-amino acids are somewhat resistant to breakdown by protein digesting enzymes because they do not have the chirality to fit in the active sites of these enzymes.

All naturally occurring sugars including the sugars that occur in DNA are of D configuration. The enzyme present in yeast can specifically ferment D-glucose and not its L-enantiomer.

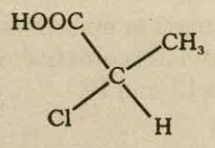
Stereochemistry also plays an important role in deciding the physiological properties of compounds. (–)-Nicotine is much more toxic than (+)-Nicotine, (+)-adrenaline is very active in constriction of blood vessels than (–)-adrenaline.

CHEMICAL RESOLUTION OF A RACEMIC ACID

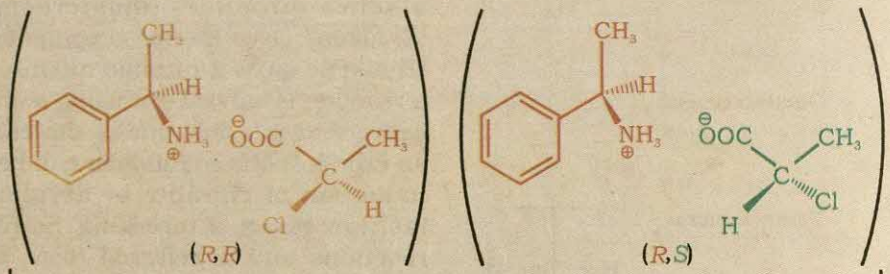


(R)-1-Phenylethylamine
(an optically pure reagent
-a resolving agent; it is reacted
with the racemic mixture)

+



2-Chloropropanoic acid
(racemic mixture, R + S)



(*R*,*R*) (*R*,*S*)

Mixture of diastereomers : Components of the mixture have different physical properties; hence can be easily separated.

Separate the diastereomers by an appropriate method (e.g. recrystallisation)

(*R*,*R*) + (*R*,*S*)

Enantiomers *R*, and *S* are cleaved from respective diastereomers

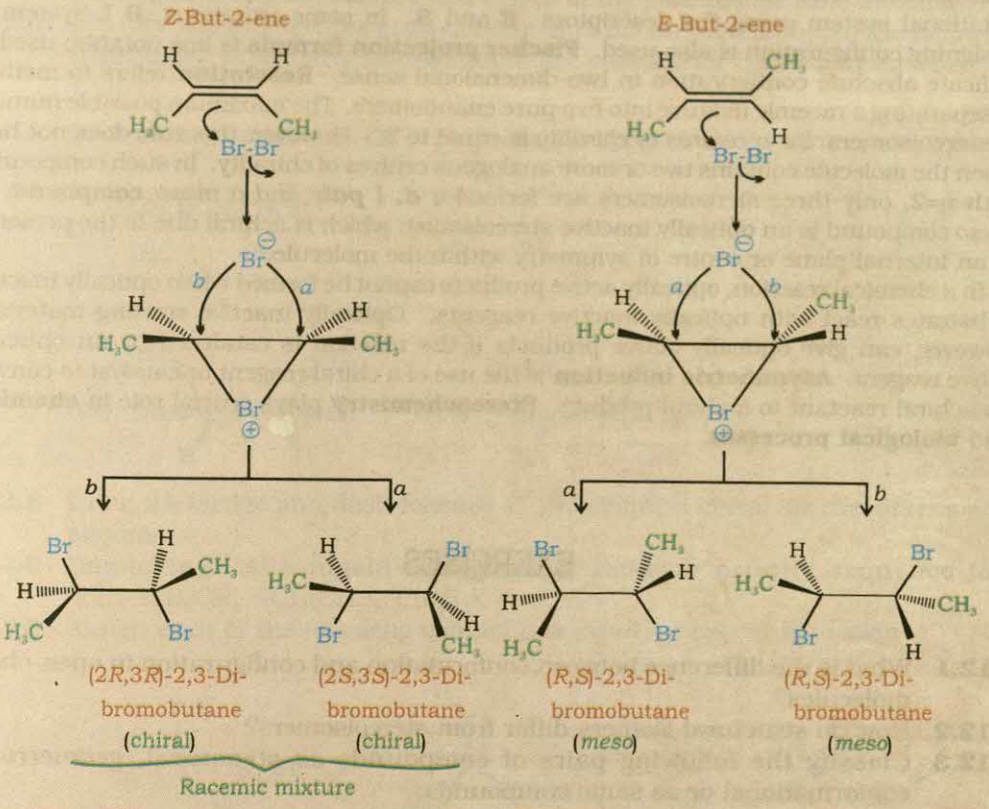
R + *R* & *R* + *S*

Resolving agent *R* is separated and recovered. Pure enantiomers from the racemate are obtained

(*R*) (*S*)

Chirality is crucial for the effect of drugs as well. In a majority of cases, only one enantiomer is found to have the desired effect while the other isomer may be totally inactive or has an opposite effect. For example, it is the (*S*)-enantiomer of ibuprofen that has the pain relieving action. (–)-Thyroxine, an amino acid of thyroid gland speeds up metabolic processes and causes nervousness and loss of weight. Its enantiomer, (+)-thyroxine, has none of this effects but is used to lower the cholesterol levels.

ADDITION OF BROMINE TO BUT-2-ENE : STEREOCHEMICAL CONSIDERATIONS



Anti addition of bromine to (*Z*) - and (*E*) -but-2-ene.The bromonium ions react with bromide ion equally by paths *a* and *b* giving racemic mixture in case of (*Z*)isomer, and a *meso* compound in case of (*E*)-isomer.

SUMMARY

The spatial arrangement of atoms or groups of atoms in a molecule is the subject matter of **Stereochemistry**. **Stereoisomers** are compounds that have same sequence of covalent bonds but differ in the relative dispositions of their atoms in space. **Conformational** and **configurational isomers** are the two main sub-classes of stereoisomers. Conformational isomers can be interconverted simply by σ-bond rotations, while configurational isomers can be interconverted only by breaking and reforming of bonds. **Geometrical** and **optical isomers** are the two important types of configurational isomers. The optical isomers rotate the plane of **plane-polarised light**. A sp^3-hybridised carbon atom bearing four different types of substituents is called an **asymmetric centre** or **chiral centre**. Chiral molecules do not possess any of the elements of symmetry. A chiral object or molecule cannot be superimposed on its mirror image. Molecules that have a plane or a centre of

symmetry are superimposable on their mirror images and are **achiral**. Stereoisomers that are mirror images of each other are called **enantiomers**. The stereoisomers that are not mirror images of each other are called **diastereomers**. A chiral molecule is **optically active**, i.e., it can rotate the plane of plane-polarised light. The enantiomer that rotates the plane of polarised light in the clockwise direction is called **dextrorotatory** (denoted as *d* or preferably as (+); and, the one that rotates plane-polarised light in the anti-clockwise sense is called **laevorotatory** [denoted as *l* or preferably as (–)].

A **racemic mixture** is optically inactive and contains equal amounts of both the enantiomers. The configuration of a chiral centre is specified by **Cahn-Ingold-Prelog** notational system using the descriptors ***R*** and ***S***. In some situations, **D L** system of assigning configuration is also used. **Fischer projection formula** is line notation used to indicate absolute configuration in two-dimensional sense. **Resolution** refers to method of separating a racemic mixture into two pure enantiomers. The maximum possible number of stereoisomers for *n centres of chirality* is equal to 2^n. However, this rule does not hold when the molecule contains two or more analogous centres of chirality. In such compounds with n=2, only three stereoisomers are formed-a ***d, l pair*** *and a* ***meso compound***. A *meso* compound is an optically inactive stereoisomer, which is achiral due to the presence of an internal plane or centre of symmetry within the molecule.

In a chemical reaction, optically active products cannot be formed when optically inactive substrates react with optically inactive reagents. Optically inactive starting materials, however, can give optically active products if the reaction is catalysed by an optically active reagent. **Asymmetric induction** is the use of a chiral reagent or catalyst to convert an achiral reactant to a chiral product. **Stereochemistry** plays crucial role in **chemical** and **biological processes**.

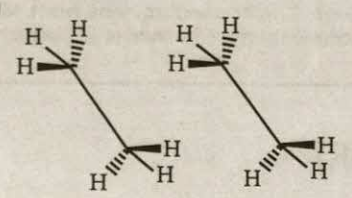
EXERCISES

12.1 What is the difference between conformation and configuration in open-chain molecules?

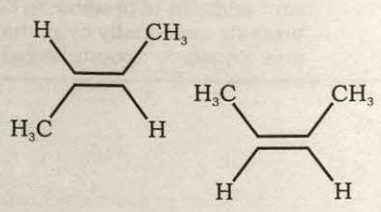
12.2 How do structural isomers differ from stereoisomers?

12.3 Classify the following pairs of compounds as structural, geometrical, conformational or as same compounds:

(a)



(b)



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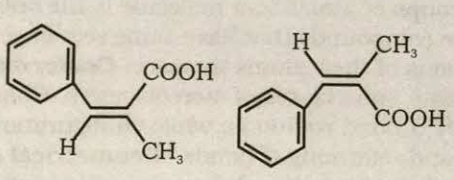
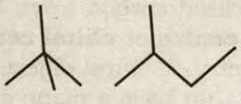


(d)

(e)



(f)

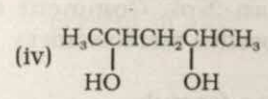
12.4 Explain the terms (i) plane-polarised light, (ii) optical activity, (iii) mirror plane, (iv) centre of inversion, (v) asymmetric molecule, (vi) super-imposable mirror images and (vii) *R* and *S* notations.

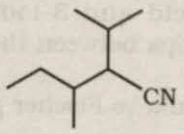
12.5 Point out the difference between (i) α_{obs} and $[\alpha]_D$, (ii) chirality and chiral centre, (iii) enantiomers and diastereomers, (iv) racemic modification and *meso* compound.

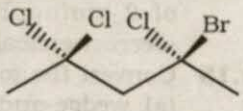
12.6 What would be the α_{obs}, if (i) concentration of a sample and (ii) length of the polarimeter tube are doubled? Will specific rotation also change if the concentration of the sample and length of the polarimeter tube are changed?

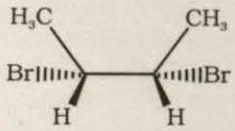
12.7 Identify and indicate the presence of centre of chirality, if any, in the following molecules. How many stereoisomers are possible for those containing chiral centre?

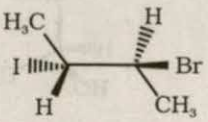
(i) 2-aminobutane (ii) 1,2-dichloropropane (iii) 3-bromo-pent-1-ene

(iv) 

(v) 

(vi) 

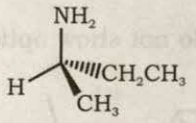
(vii) 

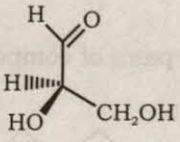
(viii) 

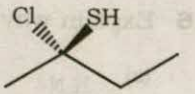
12.8 Draw the wedge and dash formula of the simplest chiral alkane, alkene and alkyne.

12.9 Employing Cahn-Ingold-Prelog rules, indicate priority sequence for: $-CH_3$, $-CH_2CH_3$, $-CH(CH_3)_2$, $C(CH_3)_3$

12.10 Assign each of the following compounds an (*R*) or (*S*) configuration

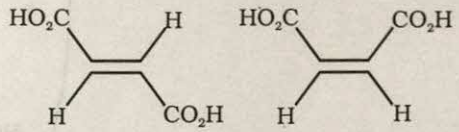
(a) 

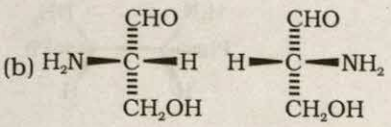
(b) 

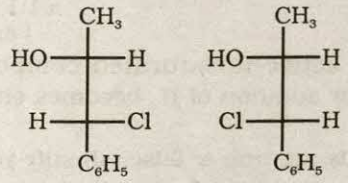
(c) 

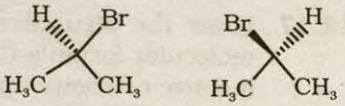
12.11 Draw three-dimensional representation of (*R*)- and (*S*)-butan-2-ol.

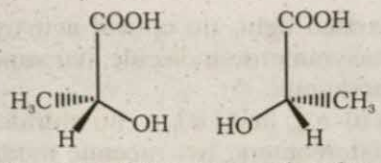
12.12 For each of the following pairs of structures, identify the relation between them. (Are they structural isomers, enantiomers, or diastereomers?)

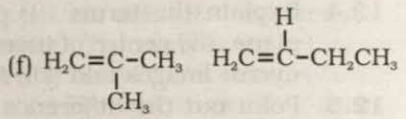
(a) 

(b) 

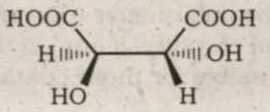
(c) 

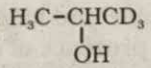
(d) 

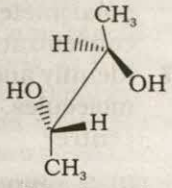
(e) 

(f) 

12.13 Which of the following molecules will show optical activity? Justify your answer.

(a) 

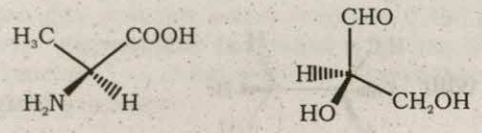
(b) 

(c) 

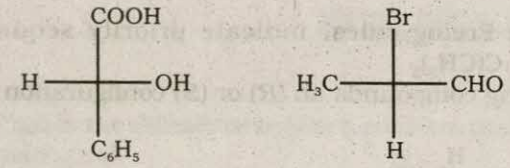
12.14 Draw wedge-and-dash and Fischer projections of all the possible stereoisomers of 2-aminopropanoic acid and 3-iodo-pentan-2-ol. Comment on the stereochemical relationships between their respective stereoisomers.

12.15 Convert the following:

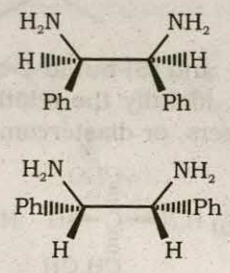
(a) wedge-and-dash formula to Fischer projection formula.

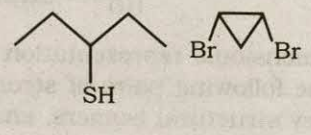


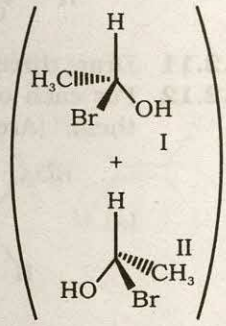
(b) Fischer projection formula to wedge and dash formula.



12.16 Explain why the following pairs of compounds do not show optical activity?

(a) 

(b) 

(c) 

a 1:1 Mixture of I and II

12.17 Draw the structures of optically active unsaturated compound having molecular formula C_5H_9Br, that after addition of H_2 becomes either optically inactive or shows optical activity.

12.18 State whether the following statements are true or false. Justify your answer.

(a) A molecule having *R* configuration is always dextrorotatory.

(b) A molecule can be optically inactive despite having centres of chirality.

(c) Optically active products can be formed if optically inactive substrates react with optically active reagents.
(d) In chemical reactions, if *S* configuration of a stereoisomer having one chiral centre is converted to *R* configuration, it always means that an inversion of configuration has occurred.
(e) A racemic mixture cannot rotate the plane of plane-polarised light.
(f) The structure lacking asymmetric centre is always achiral.
(g) If the configurational specifications like *D* and *L* or *R* and *S* are known, it is possible to predict which way a molecule will rotate the plane of plane-polarised light.
(h) The notation *(dl)* is an indicator of an optically inactive racemic modification.

12.19 Make molecular models of:
(i) 2-chloropropane and lactic acid ($CH_3CHOHCOOH$) and verify that the former is an achiral and latter is a chiral molecule.
(ii) 2,3-dihydroxybutanoic acid and 2, 3-butane-diol, and identify the diastereomeric and *meso* forms. Try to locate the elements of symmetry present, if any.

UNIT 13

ORGANIC COMPOUNDS WITH FUNCTIONAL GROUPS CONTAINING OXYGEN-I (ALCOHOLS, PHENOLS AND ETHERS)

OBJECTIVES

After studying this Unit, you will be able to:

- name alcohols, phenols and ethers according to IUPAC system of nomenclature.
- describe and explain the reactions involved in the preparation of alcohols from (1) aldehydes and ketones (2) carboxylic acids, (3) alkenes, and (4) Grignard reagents.
- describe and explain the reactions involved in the preparation of phenols from (1) aryl sulphonic acids, (2) haloarenes, and (3) diazonium salts.
- describe and explain the reactions used in preparation of ethers from (1) alcohols, (2) alkyl halides and sodium alkoxide/aryloxide.
- correlate properties of alcohols, phenols and ethers with their structures.
- describe the chemistry of commercial methods of preparation and important uses of methanol, ethanol, ethane – 1, 2 – diol, propane–1,2,3 – triol and phenol.
- name a few commercially important ethers and their uses.

"Chemistry can make compounds to cure disease, control pests and promote well-being."

In Class XI, you have studied that functional groups present in organic compounds are constituted of one or more of the following elements: carbon, hydrogen, oxygen, nitrogen, sulphur and halogens. The important classes of compounds with functional groups containing oxygen are alcohols, phenols, ethers, aldehydes, ketones, carboxylic acids and their derivatives (Table 14.4, Class XI). In this Unit, we shall discuss the chemistry of three classes of compounds, namely (i) alcohols, (ii) phenols, and (iii) ethers.

An alcohol contains one or more hydroxyl (OH) group(s) directly attached to aliphatic carbon atom(s), while a phenol contains –OH group(s) directly attached to an aryl carbon atom(s). In an ether, an oxygen atom is attached to two carbon atoms of two alkyl or an alkyl and an aryl or two aryl groups. The simplest examples of an alcohol, phenol and ether, are methanol (CH_3–OH), phenol (C_6H_5–OH) and methoxymethane (CH_3– O – CH_3), respectively.

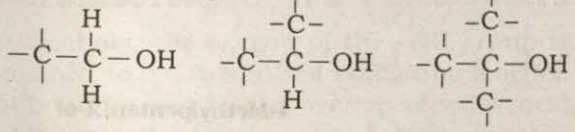
A number of compounds included under these three classes find important applications in day-to-day life as well as in industry. For example, ethanol (C_2H_5OH), a simple alcohol, is widely used as an antiseptic in the form of rectified spirit; it is an important component of all alcoholic beverages; and is widely used as a solvent for lacquers and varnishes. Simple phenol (C_6H_5OH) is an antiseptic. A phenolic compound, hexachlorophene is a constituent of several mouthwashes, deodorant soaps and medicinal skin cleansers. The simple ether, ethoxyethane ($C_2H_5OC_2H_5$) has been used as an anaesthetic for a long time. It is also widely used as a solvent and as reaction medium.

Some alcohols, phenols and ethers occur in nature and are used in the manufacture of perfumes and flavours due to their pleasant odours. For example, the fragrance of flowers such as rose and geranium is due to unsaturated alcohols, citronellol, $[(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}CH(CH_3){-}CH_2{-}OH]$ and geraniol, $(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH{-}CH_2OH$, respectively.

Alcohols are also used as starting materials for the synthesis of other classes of organic compounds such as alkanes, haloalkanes, ethers, aldehydes, ketones, acids, etc. Phenols (phenol and cresols) are used in the manufacture of dyes and resins (bakelite). We will now discuss the chemistry of these classes of compounds.

13.1 CLASSIFICATION

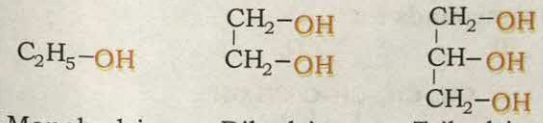
Alcohols are classified as primary, secondary or tertiary according to the carbon that bears the –OH group.



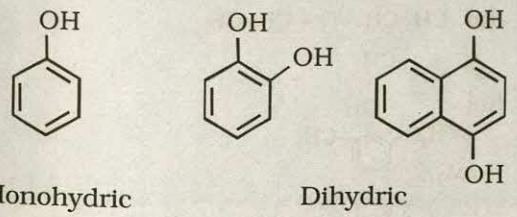
Primary Secondary Tertiary

In primary alcohols, only one carbon atom is attached to the carbon carrying the – OH group, e.g., ethanol (CH_3CH_2OH). In secondary alcohols, two carbon atoms are attached to the carbon carrying the –OH group, e.g., propan–2–ol ($CH_3{-}CH(OH){-}CH_3$). In tertiary alcohols, three carbon atoms are attached to the carbon carrying the –OH group, e.g., 2–methylpropan –2–ol ($CH_3{-}C(CH_3)(OH){-}CH_3$).

Alcohols and phenols are also classified as mono, di, trihydric as per one, two or three –OH groups present in a molecule.



Monohydric Dihydric Trihydric



Monohydric Dihydric

Ethers are known as *simple* or *symmetrical*, if the two alkyl or aryl groups attached to the oxygen atom are same, and *mixed* or *unsymmetrical*, if the two groups are different. $C_2H_5OC_2H_5$ is simple or *symmetrical* ether and $C_2H_5OCH_3$ or $C_2H_5OC_6H_5$ is a mixed or *unsymmetrical* ether.

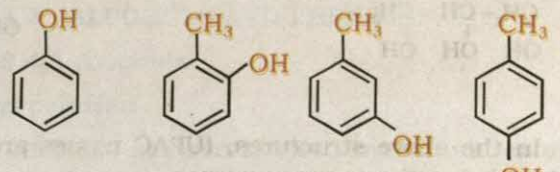
13.2 NOMENCLATURE

(i) Alcohols

Simple alcohols are known by their common names derived by adding the word alcohol after the name of the alkyl group to which the hydroxyl group is attached. For example, CH_3OH is methyl alcohol. According to IUPAC system, alcohols are named by replacing the suffix *e* in the names of alkanes by *ol* as described in Unit 14, Class XI. For naming polyhydric alcohols, the name of the alkane is retained and the ending *–e* is not dropped. The positions of carbon atoms carrying –OH groups are indicated by locants written after the name of alkane. The number of hydroxyl groups is indicated by adding the multiplicative prefix di, tri, tetra, etc., before the suffix *–ol*. Table 13.1 gives common and IUPAC names of a few selected alcohols.

(ii) Phenols

The simplest hydroxyl derivative of benzene is phenol which is also its accepted IUPAC name. The hydroxyl derivatives of toluene are o-, m- and p-cresol.

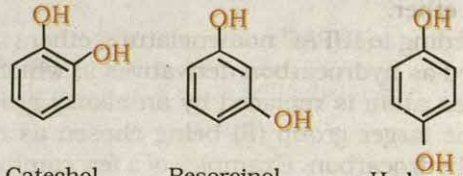


Phenol o-cresol m-cresol p-cresol

IUPAC names

Phenol 2-Methyl-phenol 3-Methyl-phenol 4-Methyl-phenol

Dihydroxy derivatives of benzene are known as 1,2-, 1,3- and 1,4-benzenediol.



Catechol 1,2-Benzenediol Resorcinol 1,3-Benzenediol Hydroquinone 1,4-Benzenediol

Table 13.1 Common and IUPAC Names of Some Alcohols

Compound	Common Names	IUPAC Names
CH_3OH	Methyl alcohol	Methanol
C_2H_5–OH	Ethyl alcohol	Ethanol
CH_3–CH_2–CH_2–OH	n-Propyl alcohol	Propan-1-ol
CH_3–CH(OH)–CH_3	Isopropyl alcohol	Propan-2-ol
CH_3–CH_2–CH_2–CH_2–OH	n-Butyl alcohol	Butan-1-ol
CH_3–CH(OH)–CH_2–CH_3	*sec.*-Butyl alcohol	Butan-2-ol
CH_3–CH(CH_3)–CH_2OH	Isobutyl alcohol	2-Methylopropan-1-ol
CH_3–C(CH_3)(CH_3)–OH	*ter*- Butyl alcohol	2-Methylpropan-2-ol
CH_3–CH(CH_3)–CH_2–CH(OH)–CH_3	—	4-Methylpentan-2-ol
CH_2(OH)–CH_2(OH)	Ethylene glycol	Ethane-1,2-diol
CH_3–CH(OH)–CH_2–CH_2(OH)		Butane -1,3-diol
CH_2(OH)–CH(OH)–CH_2(OH)	Glycerol	Propane -1,2,3-triol

In the above structures, IUPAC names are given below the common names.

(iii) Ethers

Common names of ethers follow after the names of alkyl/aryl groups written as separate words in alphabetical order. The word **ether** is added at the end. For example, $CH_3OC_2H_5$ is ethyl methyl ether.

According to IUPAC nomenclature, ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an alkoxy group –OR, the larger group (R) being chosen as the parent hydrocarbon. Examples of a few common names and IUPAC names are given in Table 13.2.

Example 13.1
Give IUPAC names of the following compounds :

(i) CH_3–CH_2–CH(CH_3)–C(CH_3)(CH_3)–CH_2OH

(ii) CH_3–CH(CH_3)–O–CH_2–CH_3

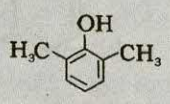
(iii) 

Table 13.2: Common and IUPAC names of some ethers

Compound	Common Names	IUPAC names
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OC_3H_7$	Methyl n- propyl ether	1-methoxypropane
$C_6H_5OC_2H_5$	Ethyl phenyl ether	Ethoxybenzene
$C_6H_5OC_7H_{15}$	Heptyl phenyl ether	1-Phenoxyheptane
$CH_3O-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$	—	2-Methoxypropane
$C_6H_5-O-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$	—	3- (Methylbutoxy) benzene
CH_3-O-CH_2-CH_2-OCH_3	—	1,2-Dimethoxyethane

Solution

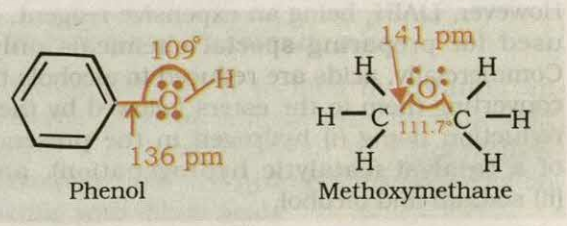
(i) 2,2,3-Trimethylpentan-1-ol
(ii) 2-Ethoxypropane
(iii) 2,6-Dimethylphenol

13.3 STRUCTURES OF FUNCTIONAL GROUPS

In alcohols, the oxygen of the –OH group is attached to sp^3 hybridised carbon by a sigma (σ) bond formed by the overlap of sp^3 hybrid orbital of carbon with an sp^3 hybrid orbital of oxygen. Fig. 13.1 illustrates bonding in methanol.

The bond angle $\overset{\frown}{C-O-H}$ in alcohols is slightly less than the tetrahedral angle (109°-28′). It is due to the repulsion between the unshared electron pairs of oxygen. In phenols, the –OH group is attached to sp^2 hybrid carbon of an aromatic ring. The bond angle $\overset{\frown}{C-O-H}$ in phenol is 109°. The carbon–oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring.

In ethers, the four electron pairs, i.e., the two bond pairs and two lone pairs of electrons around oxygen are arranged approximately in a tetrahedral arrangement. The bond $\overset{\frown}{C-O-C}$ angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (-R) groups. The C-O bond length (141 pm) in ethers is almost the same as in alcohols.



13.4 ALCOHOLS AND PHENOLS

13.4.1 Alcohols

Preparation

Alcohols are synthesised by a number of methods.

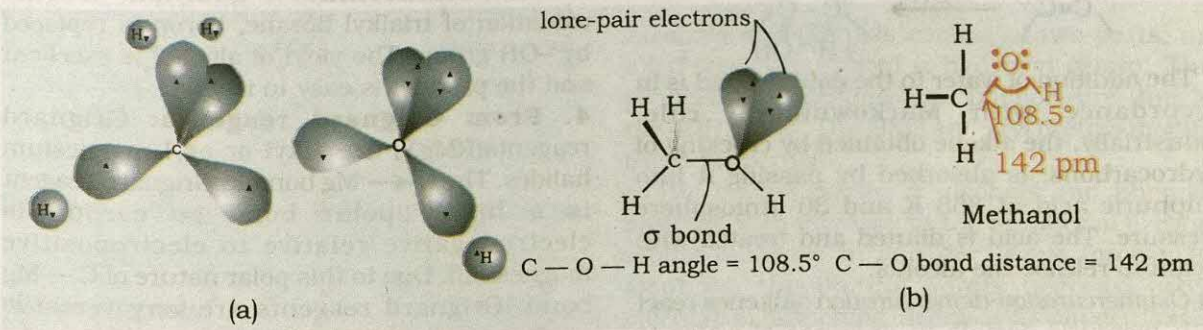


Fig. 13.1 *Methanol is formed by the formation of a bond resulting due to the overlap of an sp^3 orbital of carbon of $-CH_3$ and an sp^3 orbital of oxygen of –OH group.*

1. From Aldehydes and Ketones: Aldehydes and Ketones are reduced to the corresponding alcohols by (a) addition of hydrogen in the presence of catalysts (catalytic hydrogenation), such as finely divided platinum, palladium, nickel and ruthenium, and (b) treating aldehydes and ketones with chemical reagents such as sodium borohydride [sodium tetrahydridoborate (III),$NaBH_4$] or lithium aluminiumhydride [lithium tetrahydrido-aluminate (III), $LiAlH_4$]. Aldehydes yield primary alcohols while ketones give secondary alcohols.

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$$

$$RCOR' \xrightarrow[(ii)\ H_2O]{(i)\ NaBH_4} R\text{-}\underset{OH}{CH}\text{-}R'$$

2. From carboxylic acids and esters: Carboxylic acids are reduced to primary alcohols in presence of strong reducing agent, lithium aluminium hydride.

$$R\,COOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2OH$$

The alcohol is obtained in excellent yield. However, $LiAlH_4$ being an expensive reagent, is used for preparing special chemicals only. Commercially, acids are reduced to alcohols by converting them to the esters followed by their reduction using (i) hydrogen in the presence of a catalyst (catalytic hydrogenation), and (ii) sodium and alcohol.

$$RCOOH \quad RCOOR' \xrightarrow[Catalyst]{H_2} RCH_2OH + R'OH$$

3. From alkenes

(i) *Hydration*: Alkenes undergo hydration (addition of water across C=C bond) in presence of dilute H_2SO_4 to produce alcohols.

$$\text{>C=C<} \xrightarrow{HOH} \text{>}\underset{H}{C}\text{-}\underset{OH}{C}\text{<}$$

The addition of water to the double bond is in accordance with Markownikov's rule. Industrially, the alkene obtained by cracking of hydrocarbons, is absorbed by passing it into sulphuric acid at 353 K and 30 atmosphere Pressure. The acid is diluted and treated with steam to release the alcohol.

(ii) *Oxymercuration-demercuration* : Alkenes react with mercuric acetate in presence of water to yield hydroxy mercurial compounds. These are reduced to alcohols by sodium borohydride.

$$\text{>C=C<} + Hg(OAc)_2 + H_2O \longrightarrow \text{>}\underset{HO}{C}\text{-}\underset{HgOAc}{C}\text{<}$$

$$\xrightarrow{NaBH_4} -\underset{HO}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}-H$$

The reaction is quite fast and produces the alcohol in high yield. The alcohol obtained corresponds to Markownikov's addition of water to an alkene.

$$CH_3\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow[(ii)NaBH_4]{(i)Hg(OAc)_2/H_2O} CH_3\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_3$$

(iii) *Hydroboration:* Diborane, B_2H_6, is an electron deficient molecule. It acts as an electrophile and reacts with alkenes to yield alkylboranes, R_3B. These are oxidised to alcohols on reaction with hydrogen peroxide in presence of alkali.

$$CH_3\text{-}CH{=}CH_2 + H\text{-}BH_2 \longrightarrow CH_3\text{-}\underset{H}{CH}\text{-}\underset{BH_2}{CH_2}$$

n-propyl borane

$$\xrightarrow{CH_3\text{-}CH{=}CH_2} (CH_3CH_2CH_2)_2BH$$

di-n-Propyl borane

$$\xrightarrow{CH_3\text{-}CH{=}CH_2} (CH_3\text{-}CH_2\text{-}CH_2)_3B$$

tri-n-Propylborane

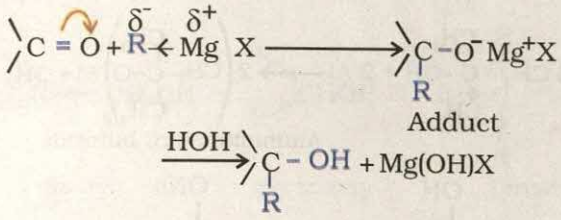
$$(CH_3\text{-}CH_2CH_2)_3B \xrightarrow{3H_2O_2/OH^-} 3CH_3\text{-}CH_2CH_2OH + B(OH)_3$$

Propan-1-ol

In each addition step, the boron atom is attached to the sp^2 carbon atom that is bonded to greater number of hydrogen atoms. The hydrogen atom is transferred from boron atom to the other carbon of double bond. Thus, it is an anti-Markovnikov's addition. During oxidation of trialkyl borane, boron is replaced by –OH group. The yield of alcohol is excellent and the product is easy to isolate.

4. From Grignard reagents: Grignard reagents(RMgX) are alkyl or aryl magnesium halides. The C$\leftarrow$ Mg bond in Grignard reagent is a highly polar bond as carbon is electronegative relative to electropositive magnesium. Due to this polar nature of C — Mg bond, Grignard reagents are very versatile reagents in organic synthesis.

Alcohols are produced by the reaction of Grignard reagents with aldehydes and ketones.

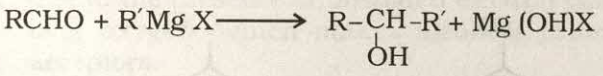


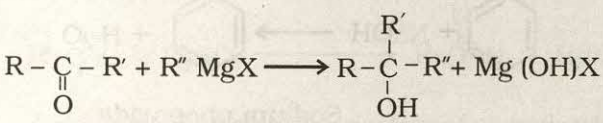
Adduct

Alcohol

The magnesium salt is converted into alcohol by treating it with water. The overall result is to bind the alkyl group of Grignard reagent to carbon of the carbonyl group and hydrogen to oxygen. Thus, the overall reactions are as follows:

$HCHO + RMgX \rightarrow RCH_2OH + Mg(OH)X$





You may note that the reaction produces a primary alcohol with HCHO, secondary alcohol with any other aldehyde, and a tertiary alcohol with a ketone.

Example 13.2

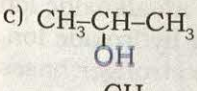
Give the structures and IUPAC names of products expected from the following reactions:

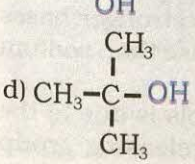
a) catalytic reduction of butanal
b) Hydroboration of but-1-ene
c) Hydration of propene in presence of dilute sulphuric acid.
d) Reaction of propanone with methyl magnesium bromide followed by hydrolysis of the adduct.

Solution

a) $CH_3–CH_2–CH_2–CH_2–OH$ Butan-1-ol

b) $CH_3–CH_2–CH_2–CH_2–OH$ Butan-1-ol

c)  Propan-2-ol

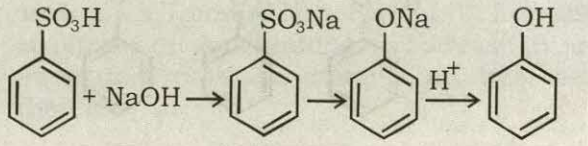
d)  2–Methylpropan-2-ol

13.4.2 Phenols

Phenol was first isolated in the early ninteenth century from coal tar. Nowadays, phenol is commercially produced synthetically. In the laboratory, phenols may be prepared from benzene derivatives by any of the following methods:

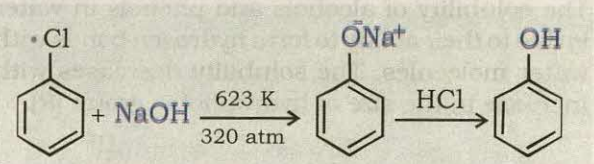
1. From aryl sulphonic acids

An aryl sulphonic acid (Unit 15, Class XI) yields the corresponding phenol on heating with molten sodium hydroxide at 570-620K



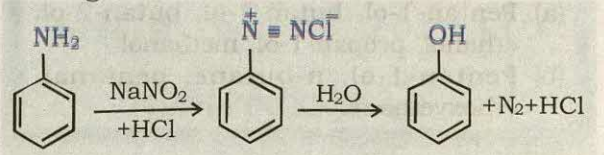
2. From haloarenes

Chlorobenzene is hydrolysed by treating it with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide.



3. Hydrolysis of diazonium salts

A diazonium salt is formed by treating an aromatic primary amine with nitrous acid ($NaNO_2$ + HCl) at 273-283 K temperature. Diazonium salts are hydrolysed to phenols on treating with dilute acids.



Aniline Benzene diazonium chloride

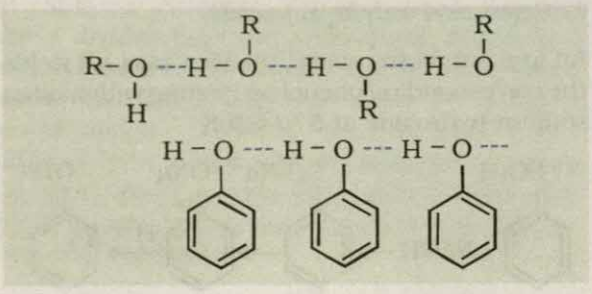
13.4.3 Physical Properties

Alcohols and phenols consist of two parts, an alkyl/aryl group and a hydroxyl group. The properties of alcohols and phenols are due to the –OH group. The alkyl and aryl groups modify these properties.

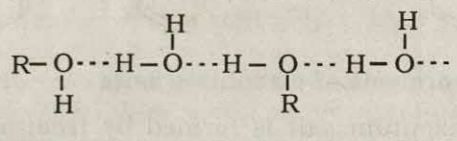
The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase in branching (decrease in van der Waals forces due to decrease in surface area).

The –OH group in alcohols and phenols contains a hydrogen bonded to an electro-negative

oxygen atom. Therefore, it is capable of forming hydrogen bond as shown below:



It is due to the presence of intermolecular hydrogen bonding that alcohols and phenols have higher boiling points than the corresponding other classes of compounds, namely, hydrocarbons, ethers and haloalkanes / haloarenes of comparable molecular masses. The solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules. The solubility decreases with increase in the size of hydrophobic group (R).



Example 13.3
Arrange the following sets of compounds in order of their increasing boiling points,
(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol
(b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

Solution
(a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol
(b) n-Butane, ethoxyethane, pentanal and pentan-1-ol.

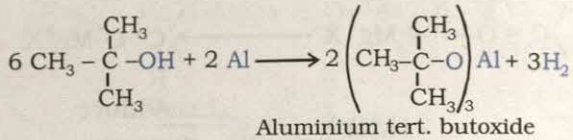
13.4.4 Chemical reactions

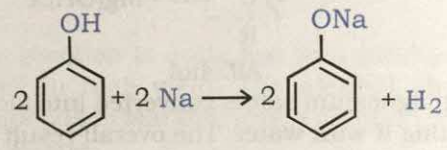
The reactions of-OH groups in alcohols and phenols may be divided into two classes:

1. Reactions involving cleavage of O–H bond

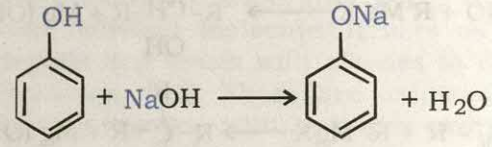
(i) *Reaction with Metals*: Alcohols and phenols react with metals such as sodium, potassium, and aluminium to yield corresponding alkoxides/phenoxides and hydrogen.

$$2R\text{-}O\text{-}H + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2RONa} + H_2$$

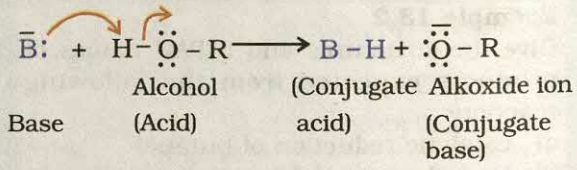




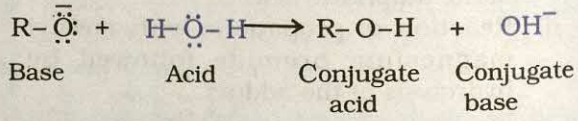
In addition to this, Phenols react with aqueous sodium hydroxide to form sodium phenoxides.



The above reactions show that alcohols and phenols are acidic in nature. In fact, alcohols and phenols are Bronsted acids i.e., they can donate a proton to a strong base (B:).

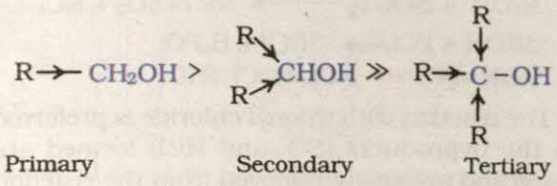


On treating an alkoxide with water, the starting alcohol is obtained.

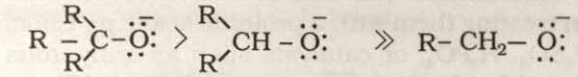


This reaction shows that water is a better proton donor than alcohol. In other words, alcohols are weaker acids than water. Also, in the above reaction, we note that an alkoxide ion is a better proton acceptor than hydroxide ion, which shows that alkoxides are stronger bases (sodium ethoxide is a stronger base than sodium hydroxide).

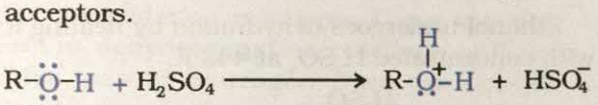
The acidic character of alcohols is due to the polar O–H bond. An electron-releasing group ($-CH_3$, $-C_2H_5$) increases electron density over the oxygen atom tending to decrease the polarity of O-H bond. This decreases the acid strength. For this reason, the acid strength of alcohols decreases in the following order:



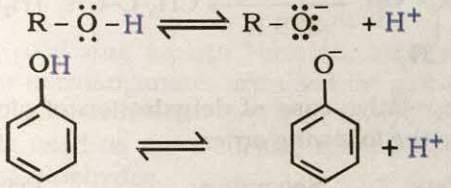
Obviously, the basic strength of their alkoxides follows the reverse order.



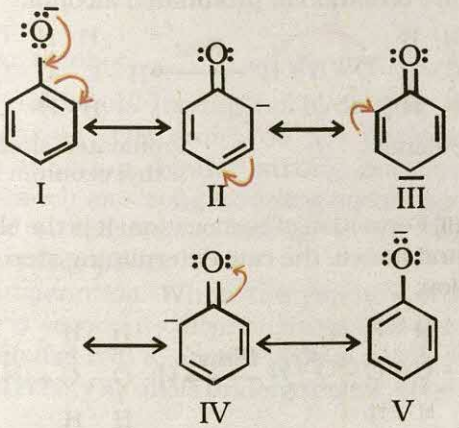
Alcohols act as Bronsted bases as well. It is due to the presence of unshared electron pairs over oxygen, which makes alcohols proton acceptors.



Acidity of Phenols: The reaction of phenols with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water. Let us examine how the hydroxyl group attached to an aromatic ring is more acidic than the hydroxyl group attached to an alkyl group. The ionisation of an alcohol and a phenol takes place as follows:



The greater acidity of phenol is due to the stability of the phenoxide ion, which is resonance stabilized as shown below.

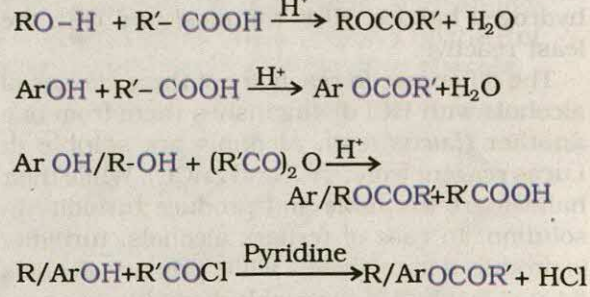


In substituted phenols, the presence of electron withdrawing groups at ortho and para positions such as nitro group, stabilizes the phenoxide ion resulting in an increase in acid strength. It is due to this reason that ortho and para nitrophenols are more acidic than phenol. On the other hand, electron releasing groups such as alkyl groups, do not favour the formation of phenoxide ion-resulting in decrease in acid strength. Cresols, for example, are less acidic then phenol.

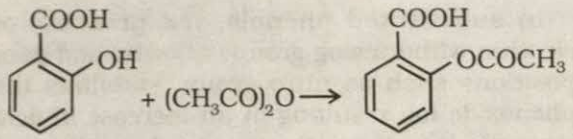
Example 13.4
Arrange the following compounds in increasing order of their acid strength: Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol

Solution
Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol, 2,4, 6-trinitrophenol.

(ii) *Esterification:* Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.



The reaction with carboxylic acid and acid anhydride is carried out in presence of a small amount of concentrated sulphuric acid. The reaction is reversible, and therefore, water is removed as soon as it is formed. The reaction with acid chloride is carried out in presence of a base (pyridine) so as to remove HCl. It also shifts the equilibrium to the right hand side. The introduction of acetyl (CH_3CO-) group in alcohols or phenols is known as **acetylation**. Acetylation of salicylic acid produces aspirin, which possesses analgesic, anti-inflammatory and antipyretic properties.



Salicylic acid — Acetyl salicylic acid (Aspirin)

2. Reactions involving cleavage of carbon – oxygen (C–O) bond

(i) *Reaction with hydrogen halides*: Alcohols react with hydrogen halides according to the following equation:

$$ROH + HX \longrightarrow R\text{–}X + H_2O$$

The alcohol may be primary, secondary, or tertiary, and hydrogen halide may be HCl, HBr or HI. For example:

(i) $CH_3CH_2CH_2OH + HI \longrightarrow CH_3CH_2CH_2I + H_2O$

(Ii) $CH_3\text{–}\underset{\underset{OH}{|}}{CH}CH_2CH_3 + HBr \rightarrow CH_3\text{–}\underset{\underset{Br}{|}}{CH}CH_2CH_3 + H_2O$

(iii) $CH_3\text{–}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{–}OH + HCl \rightarrow CH_3\text{–}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{–}Cl + H_2O$

In this reaction, tertiary alcohols are the most and primary alcohols, the least reactive. Among hydrogen halides, HI is the most and HCl, the least reactive.

The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (*Lucas test*). Alcohols are soluble in Lucas reagent (conc. HCl and $ZnCl_2$). While their halides are insoluble and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately while primary alcohols do not produce appreciable turbidity at room temperature.

(ii) *Reaction with phosphorus trihalides :* Alcohols are converted to alkyl bromides by reaction with phosphorus tribromide.

$$3\,ROH + PBr_3 \longrightarrow 3\,RBr + H_3PO_3$$

Alkyl iodides are obtained by reacting an alcohol with iodine in presence of phosphorus.

$$ROH \xrightarrow{Red\ P + I_2} R\text{–}I$$

Alkyl chlorides are prepared by reacting an alcohol with thionyl chloride or phosphorus trichloride or phosphorus pentachloride.

$$R\text{-}OH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$$

$$3ROH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

$$ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$$

The reaction with thionyl chloride is preferred as the byproducts (SO_2 and HCl) formed are gases and are easily removed from the reaction mixture.

(iii) *Dehydration*: Alcohols undergo dehydration to form alkenes (removal of a molecule of water on treating them with a protonic acid e.g., Conc. H_2SO_4, H_3PO_4, or catalysts such as anhydrous zinc chloride or alumina, Unit 15, Class XI).

$$\underset{\underset{H\ OH}{|\ \ |}}{-C-C-} \xrightarrow[Heat]{H^+} \rangle C{=}C\langle + H_2O$$

Ethanol undergoes dehydration by heating it with concentrated H_2SO_4 at 443 K.

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

Secondary and tertiary alcohols are dehydrated under milder conditions. For example:

$$CH_3\underset{\underset{OH}{|}}{CH}CH_3 \xrightarrow[440\ K]{85\%\ H_3PO_4} CH_3\text{–}CH{=}CH_2 + H_2O$$

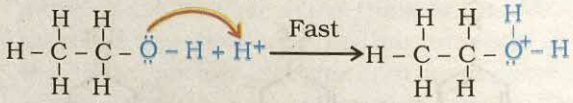
$$CH_3\text{–}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{–}OH \xrightarrow[358\ K]{20\%\ H_3PO_4} CH_3\text{–}\overset{\overset{CH_2}{\|}}{C}\text{–}CH_3 + H_2O$$

The relative ease of dehydration of alcohols follows the following order:

Tertiary alcohol > Secondary alcohol > Primary alcohol

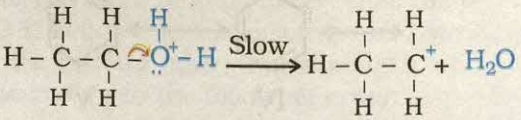
The mechanism of dehydration of ethanol involves the following steps;

Step (i) Formation of protonated alcohol:

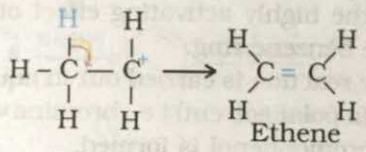


Ethanol — Protonated alcohol (Ethyl oxonium ion)

Step (ii) Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.



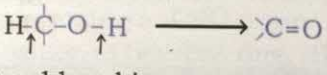
Step (iii) Formation of ethene:



Ethene

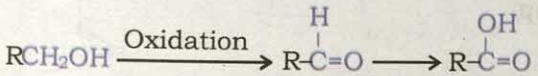
The acid used in Step (i) is finally released after the reaction.

(iv) *Oxidation* : Oxidation of alcohols involves the formation of a carbon oxygen double bond with cleavage of an O-H and C-H bonds.



Bond breaking

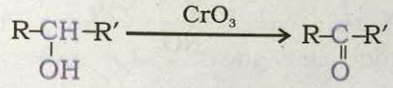
Such a cleavage and formation of bonds occurs in oxidation reactions. These are also known as **dehydrogenation** reactions as these involve loss of hydrogen from an alcohol molecule. The products of oxidation reactions depend on the nature of alcohols – primary, secondary or tertiary nature of the carbon and also the oxidising agent used. A primary alcohol may be oxidised to an aldehyde or to a carboxylic acid.



Aldehyde Carboxylic acid

Strong oxidising agents such as, acidified potassium permanganate, are used for getting carboxylic acids directly. Cr(VI) in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.

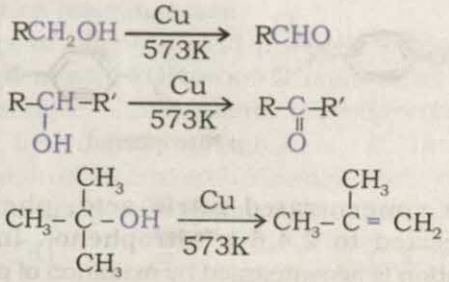
Secondary alcohols are oxidised to ketones by chromic anhyride (CrO_3).



Sec. alcohol Ketone

Tertiary alcohols having no hydrogen on carbon bearing –OH group do not undergo oxidation reaction. Under strong reaction conditions such as strong oxidizing agents and at elevated temperatures, clevage of various C-C bonds takes place.

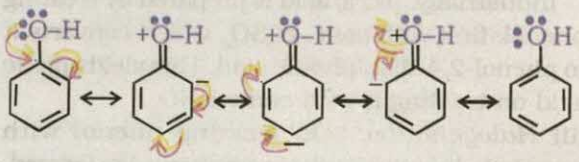
(v) *Dehydrogenation*: When the vapours of a primary or a secondary alcohol are passed over copper heated at 573 K, an aldehyde or a ketone is formed. Tertiary alcohols undergo dehydration.



Reactions of Phenols

1. Electrophilic aromatic substitution

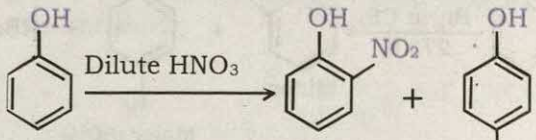
The –OH group attached to the benzene ring in phenol activates it towards **electrophilic substitution**. It also directs the incoming group to ortho and para positions in the ring as these positions become electron rich due to the electronic effect (plus mesomeric effect) caused by –OH group (Unit 15, Class XI).



I II III IV V

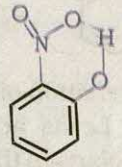
Common electrophilic aromatic substitution reactions taking place in phenol are as follows:

(i) *Nitration*: With dilute nitric acid at low temperature (298 K), phenol yields a mixture of ortho (15%) and para (30-40%) nitro phenols.

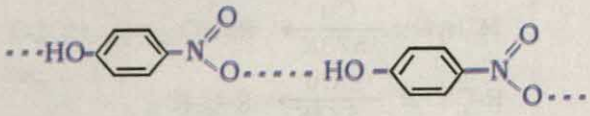


o-Nitrophenol *p*-Nitrophenol

The ortho and para isomers can be separated by steam distillation. o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.

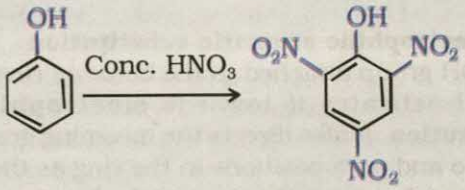


o-Nitrophenol



p-Nitrophenol

With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. In this, nitration is accompanied by oxidation of phenol.

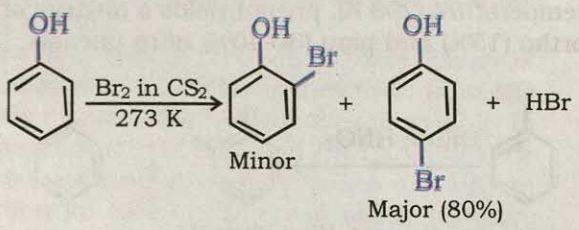


2,4,6-Trinitrophenol
(Picric acid)

Industrially, picric acid is prepared by treating phenol, first with conc. H_2SO_4 which converts it to phenol-2,4-disulphonic acid. This yields picric acid on treating it with conc. HNO_3.

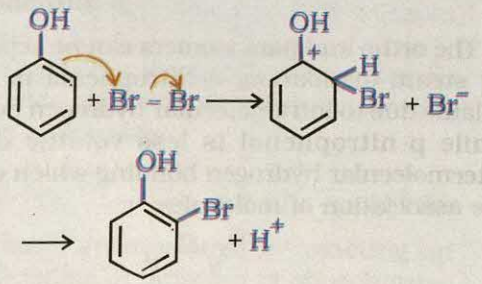
(ii) *Halogenation:* On treating phenol with bromine, different reaction products are formed.

(a) When the reaction is carried out in solvent of low polarity such as $CHCl_3$ or CS_2 and at low temperature, monobromo phenols are formed.



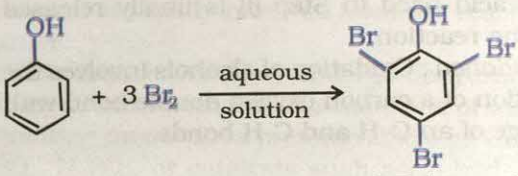
Minor

Major (80%)



The usual halogenation of benzene takes place in presence of a Lewis acid, $FeBr_3$ (Unit 15, Class XI), which polarises the halogen molecule. In case of phenol, the polarisation of bromine takes place even in the absence of Lewis acid. It is due to the highly activating effect of –OH group on the benzene ring.

(b) When the reaction is carried out in aqueous medium (a polar solvent) i.e., bromine water, 2,4,6-tribromophenol is formed.



2,4,6-Tribromophenol

Example 13.5

Write the structures of the major products expected from the following reactions:

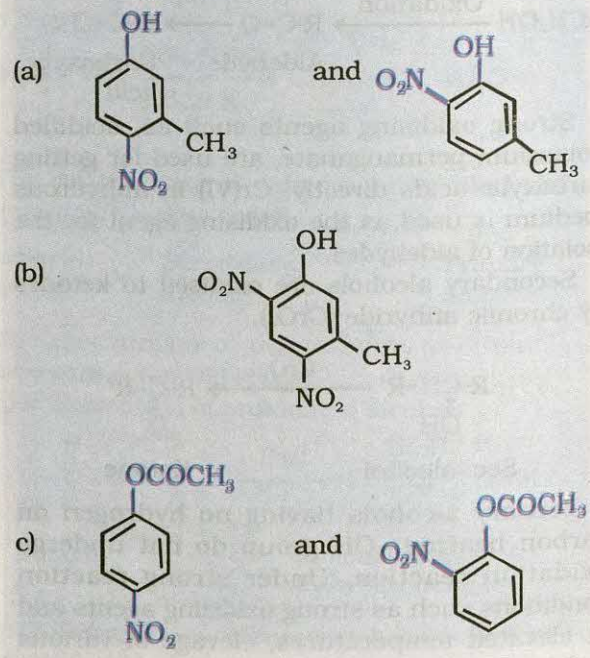
(a) Mononitration of 3-methylphenol

(b) Dinitration of 3-methylphenol

(c) Mononitration of phenyl ethanoate.

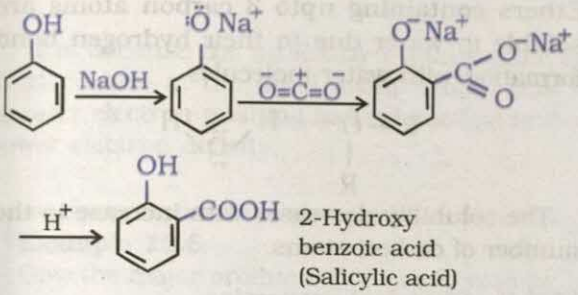
Solution

The combined influence of –OH and $-CH_3$ groups determine the position of incoming group.



2. Kolbe's reaction

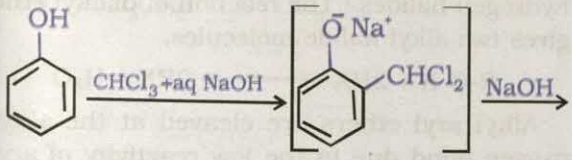
On reacting sodium salt of phenol with carbon dioxide gas, ortho hydroxybenzoic acid is formed as the main product.



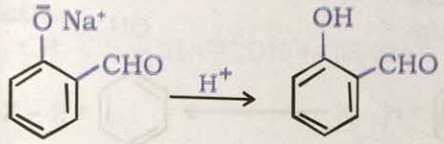
2-Hydroxy benzoic acid (Salicylic acid)

3. Reimer-Tiemann reaction

On treating phenol with chloroform in presence of sodium hydroxide, a –CHO group is introduced at ortho position of benzene ring. This reaction is known as *Reimer Tiemann reaction.*



intermediate



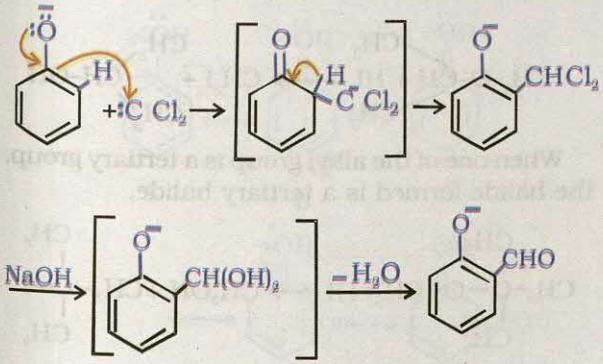
Salicylaldehyde

The intermediate substituted benzal chloride is hydrolysed in presence of alkali to produce salicylaldehyde.

It is an electrophilic substitution reaction; the electrophile dichlorocarbene, is formed by the reaction of NaOH with $CHCl_3$ or CCl_4.

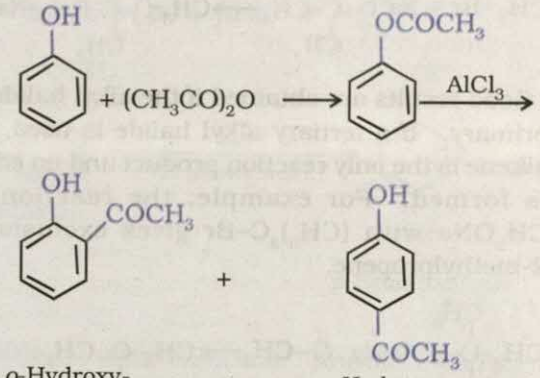
$$CHCl_3 + OH^- \rightleftharpoons H_2O + CCl_3^- \longrightarrow :CCl_2 + Cl^-$$

Dichlorocarbene contains a sextet of electrons and therefore, it is a strong electrophile.



4. Fries rearrangement

Esters of phenols yield phenolic ketones on treatment with anhydrous aluminium chloride. For example, phenyl ethanoate yields ortho- and para-hydroxyacetophenones. It involves migration of an acyl group from phenolic oxygen to ortho and para positions of the aromatic ring.



o-Hydroxy-acetophenone

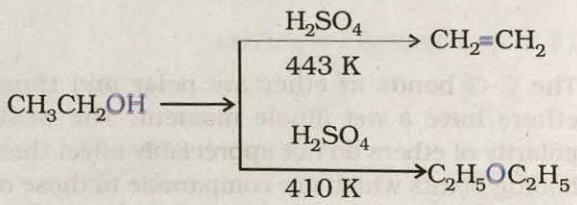
p-Hydroxy-acetophenone

13.5 ETHERS

13.5.1 Preparation

1. By dehydration of alcohols

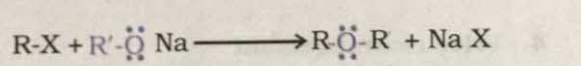
Alcohols undergo dehydration in presence of protonic acids(H_2SO_4, H_3PO_4). The formation of reaction product, alkene or ether depends on the reaction conditions. For example, ethanol is dehydrated to ethene in presence of sulphuric acid at 443 K and at 410 K; ethoxyethane is the main product.



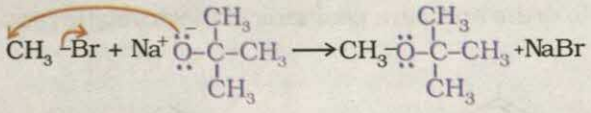
The dehydration of secondary and tertiary alcohols to get corresponding ethers is unsuccessful as alkenes are formed easily in these reactions.

2. Williamson synthesis of ethers

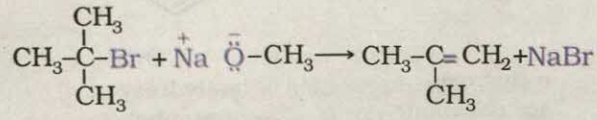
It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with a sodium alkoxide.



Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves a nucleophilic substitution of halide ion by an alkoxide ion.



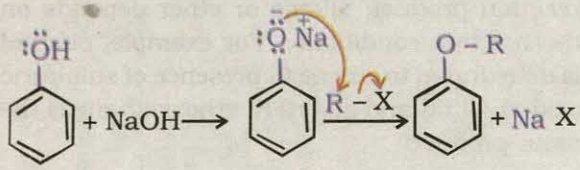
Good results are obtained if the alkyl halide is primary. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed. For example, the reaction of CH_3ONa with $(CH_3)_3C–Br$ gives exclusively 2-methylpropene.



2-methylpropene

It is because alkoxides are not only nucleophiles but also strong bases as well. They react with alkyl halides leading to elimination reactions.

Phenols are also converted to ethers by this method.



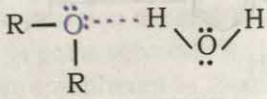
13.5.2 Physical Properties

The C-O bonds in ether are polar and thus, ethers have a net dipole moment. The weak polarity of ethers do not appreciably affect their boiling points which are comparable to those of the alkanes of comparable molecular mass but are much lower than the boiling points of alcohols (Table 13.3).

Table 13.3 Comparison of b.p.s of ether with alkane and alcohol

Compound	n-Pentane	Ethoxyethane	1-Butanol
Formula	$CH_3(CH_2)_3CH_3$	C_2H_5-O-C_2H_5	$CH_3(CH_2)_3$-OH
b.p./K	309.1	307.6K	390

Ethers containing upto 3 carbon atoms are soluble in water due to their hydrogen bond formation with water molecules.



The solubility decreases with increase in the number of carbon atoms.

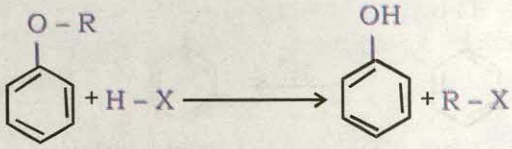
13.5.3 Chemical properties

1. Cleavage of C-O bond in ethers

Ethers are the least reactive of the functional groups. The cleavage of C-O bond in ethers takes place under drastic conditions with excess of hydrogen halides. The reaction of dialkyl ether gives two alkyl halide molecules.

$$R\text{-}O\text{-}R + 2HX \longrightarrow 2RX + H_2O$$

Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to the low reactivity of aryl-oxygen bond. The reaction yields phenol and alkyl halide.



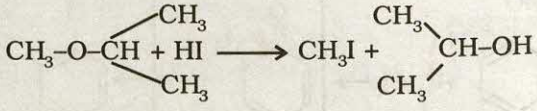
Ethers with two different alkyl groups are also cleaved in the same manner.

$$R - O - R' + HX \longrightarrow R–X + R'–OH$$

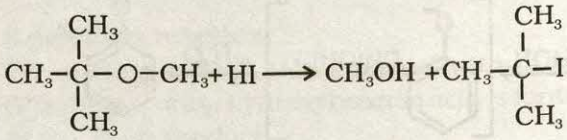
The order of reactivity of hydrogen halides is as follows: HI > HBr > HCl.

In the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide that form depend on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide. For example,

$$CH_3–O–C_2H_5 + HI \longrightarrow CH_3I + C_2H_5OH$$



When one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.



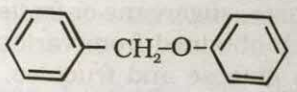
It is because the attack by I^- takes place at that carbon of the alkyl group which has a greater electron pushing inductive effect and a lower electron density.

Example 13.6

Give the major products that are formed by heating each of the following ethers with HI.

(i) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-O-CH_2CH_3$

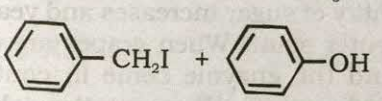
(ii) $CH_3CH_2CH_2O\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH_2CH_3$

(iii) 

Solution

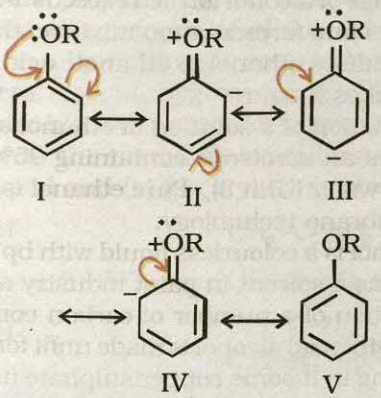
(i) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH + CH_3CH_2I$

(ii) $CH_3CH_2CH_2OH + CH_3CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-I$

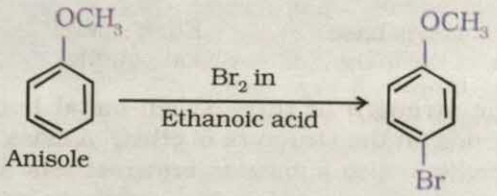
(iii) 

2. Electrophilic substitution in alkyl aryl ethers

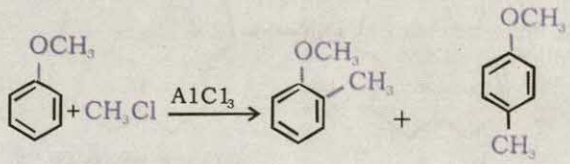
The alkoxy group (-OR) is ortho, para directing and activates the aromatic ring towards electrophilic substitution in the same way as in phenol.

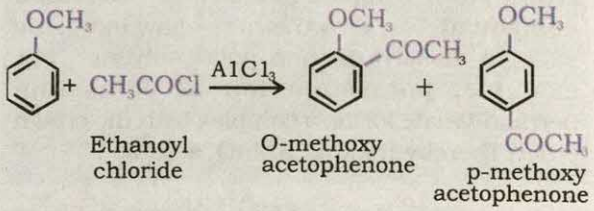


(i) *Halogenation*: Phenyl alkyl ethers undergo usual halogenation in the benezene ring, e.g., anisole undergoes bromination with bromine in ethanoic acid even in absence of iron (III) bromide catalyst. It is due to the activation of benzene ring by the methoxy group. Para isomer is obtained in 90% yield.

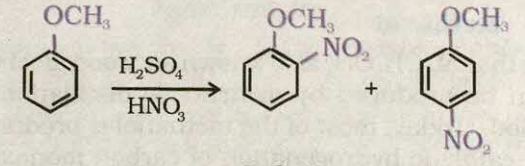


(ii) *Friedel Crafts reaction*: Anisole undergoes Friedel Crafts reaction i.e., the alkyl and acyl groups are introduced at ortho and para positions by reaction with alkyl halide and acyl halide in presence of aluminium chloride (a Lewis acid) as catalyst.



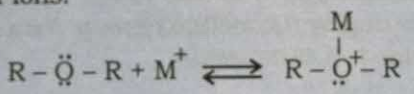


(iii) *Nitration*: Anisole reacts with a mixture of conc. H_2SO_4 and conc. HNO_3 to yield a mixture of ortho and para nitroanisole.



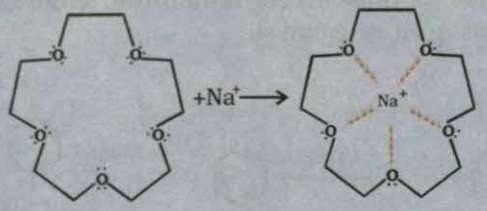
Crown Ethers

The polar nature of C-O bonds and the presence of unshared electron pairs on oxygen atom allow ethers to form complexes with metal ions.



Lewis base — Ether-metal ion complex

The strength of this oxygen-metal bond depends on the structure of ether. A class of polyethers, also known as **crown-ethers** are known to form more stable complexes with metal ions than simple ethers. Crown ethers are cyclic polyethers containing four or more ether linkages in a ring of twelve or more atoms. Crown ethers were given this name because their molecular models resemble crowns. A crown ether binds certain metal ions depending on the size of the cavity.



Host — Inclusion compound

In this reaction, the crown ether is the 'host' and the species it binds is the 'guest'. The crown-guest complex is called an **inclusion compound**. The crown ethers allow inorganic salts to dissolve in non-polar solvents. For example, potassium ion of potassium permanganate forms a complex with the crown ether, thereby making $KMnO_4$ soluble .

13.6 SOME COMMERCIALLY IMPORTANT COMPOUNDS

A few alcohols, phenols and ethers of commercial importance are discussed below:

1. Methanol

Methanol, CH_3OH, also known as 'wood alcohol', can be produced by destructive distillation of wood. Today, most of the methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature and in presence of Cu-ZnO - Cr_2O_3 catalyst.

$$CO + 2H_2 \xrightarrow[200\text{-}300\ atm,\ 573\text{-}673\ K]{Cu\text{-}ZnO\text{-}Cr_2O_3} CH_3OH$$

Methanol is a colourless liquid with bp 337 K. It is highly poisonous in nature. Ingestion of even small quantities of methanol can cause blindness and large quantities, even death. Methanol is used as a solvent in paints, varnishes and chiefly for making formaldehyde, which in turn is used as a preservative for biological specimen and for making synthetic resins.

2. Ethanol

Ethanol, C_2H_5OH, is obtained commercially by fermentation.

(i) *Fermentation*: Fermentation is the oldest method of making ethanol from sugars. The sugars in molasses, sugarcane or fruits such as grapes or starch obtained from various grains is converted to glucose and fructose, (both of which have the formula $C_6H_{12}O_6$), in presence of an enzyme invertase.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} \underset{Glucose}{C_6H_{12}O_6} + \underset{Fructose}{C_6H_{12}O_6}$$

Glucose and fructose undergo fermentation in presence of another enzyme, zymase, which is found in yeast. In wine making, grapes are the source of sugars and yeast. As grapes ripen, the quantity of sugar increases and yeast grows on the outer skin. When grapes are crushed, sugar and the enzyme come in contact and fermentation starts. Fermentation takes place in anaerobic conditions i.e. in absence of air. Carbon dioxide is released during fermentation.

$$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$$

The action of zymase is inhibited once the percentage of alcohol formed exceeds 14 percent. If air gets into fermentation mixture, the oxygen of air oxidises ethanol to ethanoic acid which in turn makes it sour.

Distillation of a solution of ethanol and water produces an azeotrope containing 95% ethanol and 5% water (Unit 3). Pure ethanol is obtained by membrane technology.

Ethanol is a colourless liquid with bp 351 K. It is used as a solvent in paint industry and in the preparation of a number of carbon compounds. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a

colour) and pyridine (a foul smelling liquid). It is known as *denaturation of alcohol.*

Nowadays, large quantities of ethanol are obtained by the hydration of ethene (Section 13.4).

3. Ethane -1,2 - diol (Ethylene glycol)

1,2-Ethanediol CH_2OH-CH_2OH, a dihydric alcohol, is prepared commercially by acid hydrolysis of epoxyethane (ethylene oxide).

$$H_2C-CH_2 \;(\text{O}) + H_2O \xrightarrow[353\ K]{H_2SO_4} HOCH_2-CH_2OH$$

1,2-Ethanediol is a colourless syrupy liquid with a high boiling point of 470 K. Its high boiling point is due to the presence of intermolecular hydrogen bonding. It shows all the reactions of -OH group. 1,2-Ethanediol is used as a coolant in automobiles. It is widely used for making dacron, -polyester used for making wrinkle free clothing (Unit 16).

4. Propane -1,2,3-triol (Glycerol)

Glycerol, HOH_2C-CHOH-CH_2OH a trihydric alcohol is present as a constituent of oils and fats in the form of triesters of long chain fatty acids. On hydrolysis in presence of an alkali, the triesters yield glycerol and salts of carboxylic acids.

$$\begin{array}{l} CH_2-O-CO-R_1 \\ | \\ CH-O-CO-R_2 \\ | \\ CH_2-O-CO-R_3 \end{array} + 3\ NaOH \longrightarrow$$

oil or fat

$$\begin{array}{ll} CH_2OH & R_1COO\ Na \\ | & + \\ CHOH & + \ R_2COO\ Na \\ | & + \\ CH_2OH & R_3COO\ Na \end{array}$$

Glycerol — Salts of fatty acids (soap)

Soaps are prepared by the saponification of oils or fats in presence of alkali. Glycerol is obtained as a by-product in soap industry. It is a colourless, viscous, hygroscopic liquid, bp 563 K. It is miscible with water and is sweet in taste. It is used in the manufacture of (a) a polyster called glyptal and (b) glyceryl trinitrate.

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3\ HNO_3 \longrightarrow \begin{array}{l} CH_2-O-NO_2 \\ | \\ CH-O-NO_2 \\ | \\ CH_2-O-NO_2 \end{array} + 3H_2O$$

Glyceryl trinitrate

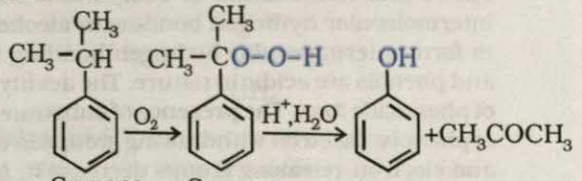
A mixture of glyceryl trinitrate and glyceryl dinitrate absorbed on kieselguhr (Porous earth) is *dynamite, an explosive.* Glycerol is also used in medicines, cosmetics and in textile processing.

Alfred Nobel

Alfred Nobel was born in Stockholm(Sweden) on October 21, 1833. Alfred developed interest in literature and basic sciences. In order to widen Alfred's horizons his father sent him abroad for training in chemical engineering. During a two year period, Alfred Nobel visited Sweden, Germany, France and the United States. In Paris, the city he liked the best, he worked in a private laboratory of Professor T. J. Pelouze, a famous chemist. There he met the young Italian chemist who, three years earlier, had invented a highly explosive liquid, nitroglycerine, produced by mixing glycerine with sulphuric and nitric acids. It was considered too dangerous to be of any practical use. After his return to Sweden from St. Petersburg in 1863, Alfred Nobel concentrated on developing nitroglycerine as an explosive. Alfred Nobel experimented with different additives and soon found that mixing nitroglycerine with silica would turn the liquid into a paste which could be shaped into rods of a size and form suitable for insertion into drilling holes. In 1867 he patented this material under the name of **dynamite**.

5. Phenol

Phenol was first isolated from coal tar. Nowadays, it is manufactured from the hydrocarbon, cumene. Cumene, isopropylbenzene is oxidised in presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid. Acetone, a by-product of this reaction, is also obtained in large quantity by this method.

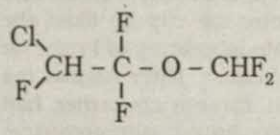


Cumene — Cumene hydroperoxide

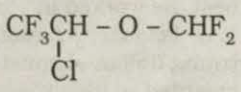
Phenol, mp 314 K, is moderately soluble in water (8% at 298 K). It is a strong antiseptic. It is widely used as a raw material for the manufacture of important dyes, drugs and pharmaceuticals, polymers, and a number of organic chemicals.

6. Ethers

The chemically unreactive nature, solvent properties and low cost of ethoxyethane make it the most important of the simple ethers. It is used as a solvent for oils, gums, resins, etc. Ethoxy ethane has also been widely used as an inhalation anaesthetic. However, because of its slow effect and unpleasant recovery period, other compounds such as ethrane and isoflurane have replaced ethoxyethane as an anesthetic. Diphenyl ether another simple ether, is used as a heat transfer medium because of its high boiling point, 531K.

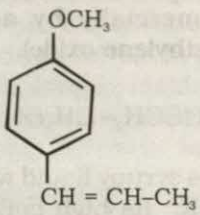


Ethrane

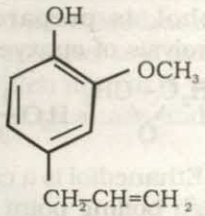


Isoflurane

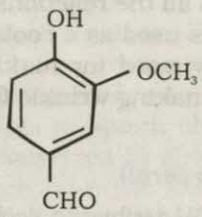
A number of naturally occurring phenols and ethers, particularly ring substituted anisoles are used as flavourings and in perfumes because of their pleasant odour. Anethole – a constituent of anise seed, eugenol – present in oil of cloves, vanillin – present in oil of vanilla bean and thymol – present in thyme and mint are examples of phenols and ethers used in perfumes and as flavourings.



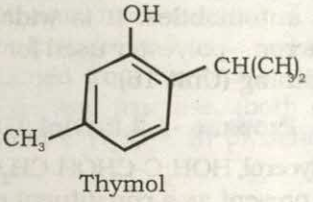
Anethole



Eugenol



Vanillin



Thymol

SUMMARY

Alcohols and phenols are compounds containing –OH as the functional group. In alcohols, the –OH group is attached to sp^3 hybridised carbon and in phenols, it is attached to sp^2 hybridised carbon of an aromatic ring. In ethers, oxygen atom is attached to two carbon atoms by two separate sigma bonds. Alcohols, phenols and ethers are systematically named according to IUPAC system of nomenclature. Alcohols may be prepared by (1)reduction of aldehydes, and ketones, (2) reduction of carboxylic acids and esters (3) from alkenes by (i) hydration, (ii)oxymercuration and (iii) hydroboration and (4) by the reaction of Grignard reagent with aldehydes and ketones. Phenols may be prepared by 1) nucleophilic substitution of (i) SO_3H group in aryl sulphonic acids, and (ii) halogen atom in haloarenes by –OH group, and 2) by hydrolysis of diazonium salts.

Alcohols are higher boiling than other classes of compounds, namely, hydrocarbons, ethers and haloalkanes of comparable molecular masses. It is due to the presence of intermolecular hydrogen bonding in alcohols. The ability of alcohols, phenols and ethers to form intermolecular hydrogen bonding with water makes them soluble in it. Alcohols and phenols are acidic in nature. The acidity of phenols is due to the resonance stablilization of phenoxide ions. The presence of substituents in the aromatic ring affects the acid strength of phenols. Electron withdrawing groups in ortho and para positions increase acidic strength and electron-releasing groups decrease it. Alcohols undergo nucleophilic substitution with hydrogen halides to yield alkyl halides. Dehydration of alcohols give alkenes. On oxidation, primary alcohols yield aldehydes with mild oxidising agents and to carboxylic acids with strong oxidising agents, secondary alcohols yield ketones. Tertiary alcohols are resistant to oxidation.

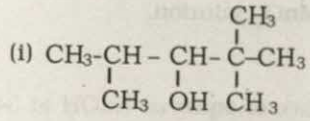
The presence of –OH group in phenols activates the aromatic ring towards electrophilic substitution (nitration, halogenation etc.) and directs the incoming group to ortho and para positions due to the mesomeric effect. Reimer Tiemann reaction of phenol yields salicylaldehyde.

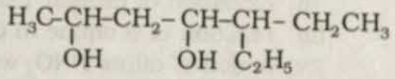
Ethers may be prepared by (i) dehydration of alcohols, and (ii) Williamson synthesis. The boiling points of ethers resemble to those of alkanes of comparable molecular mass. The C-O bond in ethers can be cleaved by hydrogen halides. In electrophilic substitution, the alkoxy group activates the aromatic ring and directs the incoming group to ortho and para positions due to mesomeric effect.

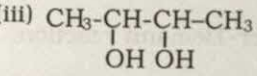
Methanol, ethanol, ethane-1,2-diol, propane-1,2,3-triol and phenol are some of the commercially important alcohols and phenols. Among ethers, ethoxyethane is a commonly used laboratory solvent. A number of naturally occurring aromatic ethers, namely, anethole, eugenol and vanillin are used as flavoring agents and in perfumes.

EXERCISES

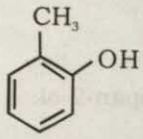
13.1 Write IUPAC names of the following compounds:

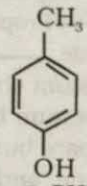
(i) 

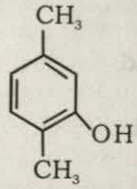
(ii) 

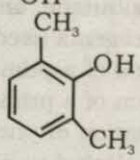
(iii) 

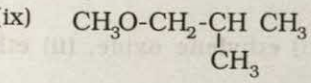
(iv) $HOCH_2–CHOH–CH_2OH$

(v) 

(vi) 

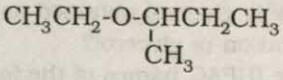
(vii) 

(viii) 

(ix) 

(x) $C_6H_5\,OC_2H_5$

(xi) $C_6H_5O\text{-}C_7H_{15}$

(xii) 

13.2 Write structures of the compounds whose IUPAC names are as follows:

(i) 2-Methylbutan- 2-ol
(ii) 1-Phenylpropan-2-ol
(iii) 3,5-Dimethylhexane-1,3,5-triol
(iv) 2,3-Diethylphenol
(v) 1-Ethoxypropane
(vi) 3-Methyl-2-ethoxypentane
(vii) Cyclohexylmethanol

13.3 Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names. Classify them as primary, secondary and tertiary alcohols.

13.4 Explain why is propanol higher boiling than butane.

13.5 Explain why are alcohols comparatively more soluble in water than the corresponding hydrocarbons.

13.6 Write equations for preparation of propan-2-ol, from (i) an alkene, and (ii) a Grignard reagent.

13.7 Write notes on (i) oxymercuration – demercuration, and (ii) hydroboration.

13.8 Give the structures and IUPAC names of monohydric phenols of molecular formula C_7H_8O.

13.9 While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which is steam distilled. Give reason.

13.10 Give the equation of the reaction of preparation of phenol from cumene.

13.11 You are given benzene, conc. H_2SO_4 and NaOH. Write the equations for the preparation of phenol using these reagents.

13.12 Give two reactions that show the acidic nature of phenol. Compare its acidity with that of ethanol.

13.13 Explain why is ortho-nitrophenol more acidic than ortho-methoxyphenol?

13.14 Explain how does the –OH group attached to a carbon of benzene ring activates it towards electrophilic substitution?

13.15 Give the equations of the following reactions:

(i) reaction of propene with mercuric acetate followed by hydrolysis

(ii) oxidation of propan-1-ol with alkaline $KMnO_4$ solution.

(iii) reaction of bromine in CS_2 with phenol

(iv) action of dilute HNO_3 with phenol

(v) treating phenol with chloroform in presence of aqueous NaOH at 343K.

13.16 Write short notes on:

(i) Kolbe reaction, and (ii) Reimer-Tiemann reaction.

13.17 How are the following conversions carried out?

(i) Propane $\longrightarrow$ Propan-2-ol

(ii) Benzyl chloride $\longrightarrow$ Benzyl alcohol

(iii) Ethyl magnesium chloride $\longrightarrow$ Propan-1-ol

(iv) Methyl magnesium bromide $\longrightarrow$ 2-Methylpropan-2-ol.

13.18 How will you prepare butan-1-ol from

(i) 1-bromobutane, and (ii) a suitable alkene ?

13.19 Name the reagents used in the following reactions:

(i) oxidation of a primary alcohol to carboxylic acid.

(ii) oxidation of a primary alcohol to an aldehyde.

(iii) bromination of phenol to 2,4,6-tribromophenol.

(iv) benzyl alcohol to benzoic acid.

(v) dehydration of propan-2-ol to propene.

(vi) butan-2-one to butan-2-ol.

13.20 How is ethane –1,2– diol prepared from (i) ethylene oxide, (ii) ethene, and (iii) 1,2-dibromoethane?

13.21 How is glycerol obtained as a by-product of soap industry? Write the equation of nitration of glycerol?

13.22 Give IUPAC names of the following ethers:

(i) $CH_3OCH_2–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_3$ (ii) $CH_3\ OCH_2CH_2Cl$

(iii) $O_2N - C_6H_4–OCH_3(p)$ (iv) $CH_3–CH_2–CH_2–OCH_3$

13.23 Write the names of reagents and equations for the preparation of the following ethers by Williamson synthesis:

(i) 1-propoxypropane (iii) 2-methyl-2-methoxypropane

(ii) Ethoxybenzene (iv) 1-methoxyethane.

13.24 Illustrate with examples the limitations of Williamson Synthesis for the preparation of certain types of ethers.

13.25 How is 1-propoxypropane synthesised from propan-1-ol?

13.26 Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

13.27 Write the equation of the reaction of hydrogen iodide with
(i)1- Propoxypropane (ii) Methoxybenzene and (iii) Benzyl ethyl ether.

13.28 Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution, and (ii) it directs the incoming substituents to ortho and para positions in benzene ring.

13.29 Write equations for the following reactions:
(i) Friedel Crafts reaction – alkylation in anisole
(ii) Nitration of anisole
(iii) Bromination of anisole in ethanoic acid medium.
(iv) Friedel Crafts acetylation of anisole.

UNIT 14

ORGANIC COMPOUNDS WITH FUNCTIONAL GROUPS CONTAINING OXYGEN-II

(Aldehydes, Ketones, Carboxylic acids and their derivatives)

OBJECTIVES

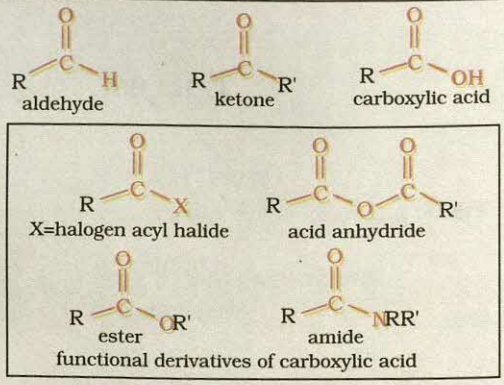
After studying this Unit, you will be able to:

- write the trivial and IUPAC names of aldehydes, ketones, carboxylic acids and their derivatives.
- write the structures of the functional groups present in the above classes of compound.
- correlate the physical properties and chemical reactivities of these classes of compounds and strengths of carboxylic acids with their structures.
- describe the important methods of their preparation and reactions.
- understand the mechanisms of nucleophilic addition and aldol condensation reactions of aldehydes and ketones and nucleophilic acyl substitution reactions.
- learn the chemistry of some commercially important members of these families of compounds.

"Acetone, known as propanone, is one of the most widely used solvents in chemical industry, the laboratory, and the home."

In the previous Unit, you have studied organic compounds with functional groups containing oxygen bonded to a carbon atom through a single bond. In this Unit you will study another class of very important oxygen containing organic compounds in which oxygen is bonded to a carbon atom through a double bond. The functional unit >C=O, present in these compounds, is called **carbonyl group**. Although a large variety of organic compounds containing a carbonyl group is possible, we shall limit our study to those compounds in which an acyl group (R–C=O) is bonded to hydrogen, carbon, oxygen, halogens and nitrogen. These compounds are known as carbonyl compounds and are grouped into families of aldehydes, ketones, carboxylic acids and their derivatives. The functional derivatives of carboxylic acids are further sub-divided into families of esters, acyl (or acid) halides, acid anhydrides and amides. The general formulae of these families of compounds are shown below. The functional groups present in these compounds are shown in red colour.

Except in ketones and esters where R and R' are alkyl or aryl groups in all the other cases R and R' may be alkyl, aryl or hydrogen.



Acid halides and anhydrides do not occur in nature due to their high reactivity. In contrast, other carbonyl compounds are widespread in plants and animals. They play important roles in biochemical processes to sustain life. They add fragrance and flavour to the Nature and constitute several pharmaceuticals. Some members of these families are manufactured in large quantities for use as solvents and for producing materials like adhesives, paints, resins, perfumes, plastics, fabrics, etc. From synthesis viewpoint, they are the most important compounds and occupy the centre stage of organic synthesis.

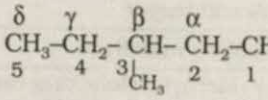
14.1 ALDEHYDES AND KETONES

Aldehydes and ketones are the simplest but most important carbonyl compounds.

14.1.1 Nomenclature

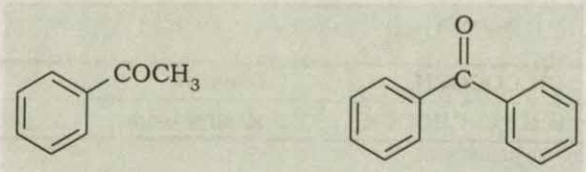
As you know, the IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending *-e* with *-al* and *-one*, respectively. The longest carbon chain containing the carbonyl carbon is taken to decide the name of the parent alkane. The carbon chain is numbered from the end nearer to the carbonyl group and the substituents are prefixed in alphabetical order along with Arabic numerals indicating their positions in the carbon chain. Since the carbon of the aldehyde group, being at the end of the carbon chain, always gets number 1, it is not necessary to indicate the position of the aldehyde group in the name. The same applies to cyclic ketones, where the carbonyl carbon is at number 1 position. When the aldehyde group is attached to a ring, the suffix carbaldehyde is added after the full name of the hydrocarbon. The numbering of the ring carbon atoms starts from the carbon atom attached to the aldehyde group. The name of the simplest aromatic aldehyde carrying the aldehyde group on a benzene ring is benzaldehyde, which is a common name accepted by IUPAC. Other ring substituted aromatic aldehydes are named as derivatives of benzaldehyde.

The trivial names of aldehydes are derived from the trivial names of the corresponding carboxylic acids (Section 14.2.1) by replacing the ending ic acid with aldehyde. The positions of the substituents in the carbon chain are indicated by Greek letters α, β, γ, δ etc., the α-carbon being the one directly linked to the aldehyde group, β-carbon the next, and so on. This is illustrated as follows:



β–Methylvaleraldehyde
(Common name)
3-Methylpentanal
(IUPAC name)

The common names of ketones are derived by adding the names of the alkyl or aryl groups directly linked to the carbonyl group before the word ketone. The simplest ketone, CH_3COCH_3, is also called acetone. The positions of the substituents are indicated by the Greek letters α, α′, β, β′ and so on; α, α′ carbons being the ones directly attached to the carbonyl group. Ketones with a carbonyl group attached to a benzene ring are also named as phenones, some of such names have been accepted by IUPAC.



Acetophenone Benzophenone

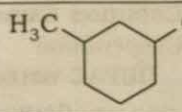
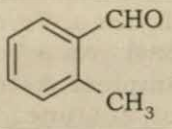
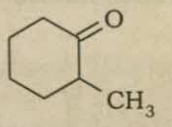
The common and IUPAC names of some aldehydes and ketones are given in Table 14.1.

Example 14.1
Write the structural formulae of all the carbonyl compounds with the molecular formula $C_5H_{10}O$ and name them according to the IUPAC system.

Solution
The molecular formula suggests open chain structures for the carbonyl compounds. The following structures are possible:

$CH_3CH_2CH_2CH_2CHO$	$CH_3CH_2CH(CH_3)CHO$
Pentanal	2-Methylbutanal
(I)	(II)
$(CH_3)_2CHCH_2CHO$	$(CH_3)_3C$-CHO
3-Methylbutanal	2,2-Dimethylpropanal
(III)	(IV)

Table 14.1 Common and IUPAC names of some aldehydes and ketones

Structure	Common Name	IUPAC Name
Aldehydes		
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$(CH_3)_2CHCHO$	Isobutyraldehyde	2-Methylpropanal
	γ -Methylcyclohexanecarbaldehyde	3-Methylcyclohexanecarbaldehyde
	o-Tolualdehyde	2-Methylbenzaldehyde
$CH_3CH=CHCHO$	Crotonaldehyde	But-2-enal
Ketones		
$CH_3COCH_2CH_2CH_3$	Methyl n-propyl ketone	Pentan-2-one
$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α -Methylcyclohexanone	2-Methylcyclohexanone
$CH_3COCOCH_3$	Diacetyl	Butane-2,3-dione
$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one

$CH_3COCH_2CH_2CH_3$
Pentan-2-one
(V)

$CH_3CH_2COCH_2CH_3$
Pentan-3-one
(VI)

$CH_3CO\text{-}CH(CH_3)_2$
3-Methylbutan-2-one
(VII)

14.1.2 Structure of the Carbonyl Group

The carbonyl carbon atom in aldehydes and ketones is sp^2-hybridized and forms three σ-bonds separated by 120° from each other. One of the σ-bonds is formed with the oxygen atom and the other two with carbon and/or hydrogen atoms. The fourth valence electron, which remains in the unhybridised *p*-orbital, overlaps with the oxygen *p*-orbital to form a π-bond. The oxygen atom has two lone pairs of electrons, which occupy its remaining two orbitals. The carbonyl carbon and the three atoms bonded to it lie in one plane and the pi-electron cloud is above and below this plane, as shown below in Fig. 14.1.

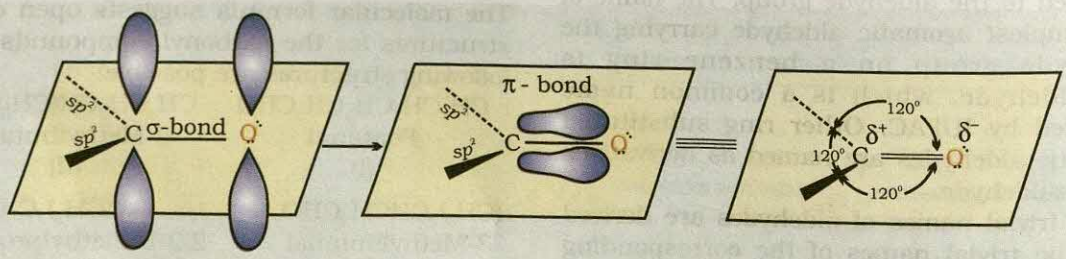
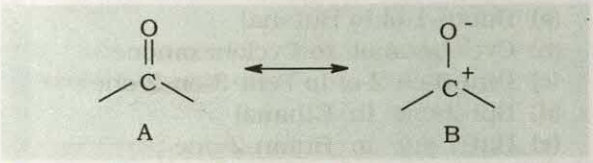


Fig. 14.1 *Orbital diagram for the formation of carbonyl group.*

The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon. The electrons, particularly the loosely held π-electrons, are pulled strongly towards the oxygen atom to give oxygen a partial negative charge and carbon a partial positive charge indicated by the symbols δ- and δ+, respectively. Thus, the carbonyl carbon is an electrophilic (Lewis acidic), and carbonyl oxygen a nucleophilic (Lewis basic) centre. Carbonyl compounds have substantial dipole moments and are more polar than ethers. For example, the dipole moments of ethanal, propanone and diethyl ether are 2.72, 2.88 and 1.18 D, respectively. The high polarity of carbonyl compounds is due to the highly polar character of the carbonyl group. The high polarity of the carbonyl group is explained on the basis of resonance involving a neutral (A) and a dipolar (B) structures as shown below:



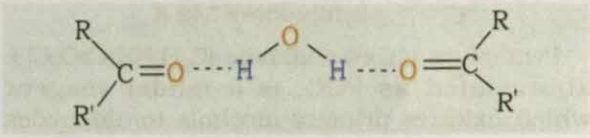
14.1.3 Physical Properties

Methanal is a gas at room temperature. Ethanal is a volatile liquid, bp 294 K. Other aldehydes and ketones are liquids or solids at room temperature. The lower aldehydes have sharp pungent odours. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones have been used in the blending of perfumes and flavouring agents.

They have higher boiling points than non-polar compounds (hydrocarbons) or weakly polar compounds (ethers) of comparable molecular masses due to intermolecular dipole-dipole attraction. However, their boiling points are lower than those of alcohols of comparable molecular masses because, unlike alcohols, they cannot form intermolecular hydrogen bonds. This is clear by comparing the boiling points of the following compounds:

	b.p.(K)	*Mol. mass*
n-Pentane	309	72
Ethoxyethane	308	74
Butanal	349	72
Butan-2-one	353	72
Butan-1-ol	391	74

The lower members of aldehydes and ketones (methanal, ethanal, propanone) are miscible with water because they form hydrogen bonds with water as shown below:



As the size of the alkyl group increases the solubility decreases rapidly. However, lower as well as higher aldehydes and ketones are freely soluble in organic solvents such as benzene, ether, methanol, etc.

Example 14.2
Arrange the following compounds in increasing order of their boiling points: CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$.

Solution: The molecular masses of these compounds are similar. However, only CH_3CH_2OH is an associated liquid due to extensive intermolecular hydrogen bonding. CH_3CHO is more polar than CH_3OCH_3. Therefore, intermolecular dipole-dipole attraction is stronger in the former. The molecules of $CH_3CH_2CH_3$ have only weak Van der Waal forces. Therefore, the following order of boiling points should be observed:

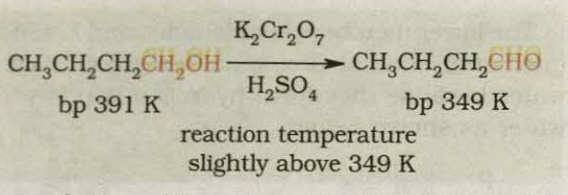
$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$.

14.1.4 General Methods of Preparation

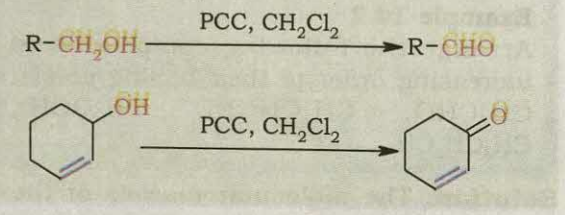
Some important methods for the preparation of aldehydes and ketones are as follows:

(A) From alcohol

(i) *By Oxidation*: Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively (Section 13.4.4). The most commonly used oxidising reagents are $KMnO_4$, $K_2Cr_2O_7$ and CrO_3. However, these are strong oxidising agents and further oxidise the aldehyde produced by the oxidation of a primary alcohol to carboxylic acid. A few primary alcohols of low molecular masses may be oxidised to aldehydes if the reaction temperature is so adjusted that the aldehyde, being lower boiling than the alcohol, distils out of the reaction mixture as soon as it is formed, thus escaping from further oxidation.



Pyridinium chloro-chromate ($C_5H_5NH^+CrO_3Cl^-$), abbreviated as PCC, is a milder reagent which oxidizes primary alcohols to aldehydes and secondary alcohols to ketones in dichloromethane solvent. *Aldehydes are not oxidised further to carboxylic acids*. Carbon-carbon double bond also remains unaffected. PCC is prepared by mixing pyridine (C_5H_5N), CrO_3 and HCl in dichloromethane.



(ii) *By Dehydrogenation*: This method is suitable for volatile alcohols and is of industrial application. In this method, alcohol vapours are passed over heated metal catalysts, such as silver or copper. Primary alcohols give aldehydes; and secondary alcohols give ketones (Section 13.4.4).

2. From acid chlorides

Acid chlorides can be reduced to aldehydes and converted to ketones. These reactions will be discussed in (Section 14.3.4).

3. From nitriles

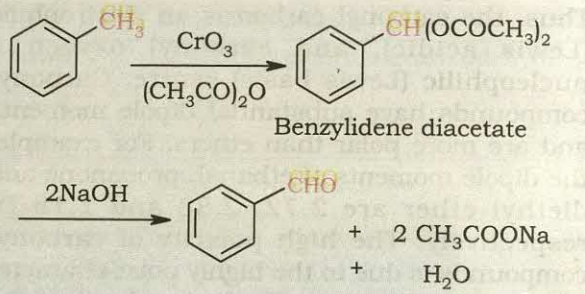
Aldehydes and ketones can be prepared from nitriles (Section 15.3.6).

4. From hydrocarbons

(i) *By ozonolysis of alkenes*: As you know, ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes, ketones or a mixture of both depending on the substitution pattern of the alkene (Class XI, Unit 15).

(ii) *By hydration of alkynes*: As you know, ethyne adds water in the presence of H_2SO_4 and $HgSO_4$ to give acetaldehyde. All other alkynes give ketones in this reaction (Class XI, Unit 15).

(iii) *By oxidation of methylbenzenes*: Oxidation of an aromatic compound having a methyl group at the benzene ring with CrO_3 in the presence of acetic anhydride followed by hydrolysis gives corresponding benzaldehyde. Further oxidation of the aldehyde is prevented because it is trapped by acetic anhydride as a non-oxidisable benzylidene diacetate derivative, which is then hydrolysed with alkali to give the aldehyde.



Example 14.3

Give the reagents to bring about the following transformations:

(a) Butan-1-ol to Butanal
(b) Cyclohexanol to Cyclohexanone
(c) Pent-3-en-2-ol to Pent-3-en-2-one
(d) But-2-ene to Ethanal
(e) But-1-yne to Butan-2-one
(f) p-Nitrotoluene to p-Nitrobenzaldehyde.

Solution

(a) $C_5H_5NH^+\ CrO_3Cl^-$ (PCC)
(b) $K_2Cr_2O_7/KMnO_4$ in acidic media
(c) PCC (d) O_3/H_2O – Zn dust
(e) Dilute H_2SO_4 – $HgSO_4$
(f) CrO_3 in presence of $(CH_3CO)_2O$

14.1.5 Chemical Reactions

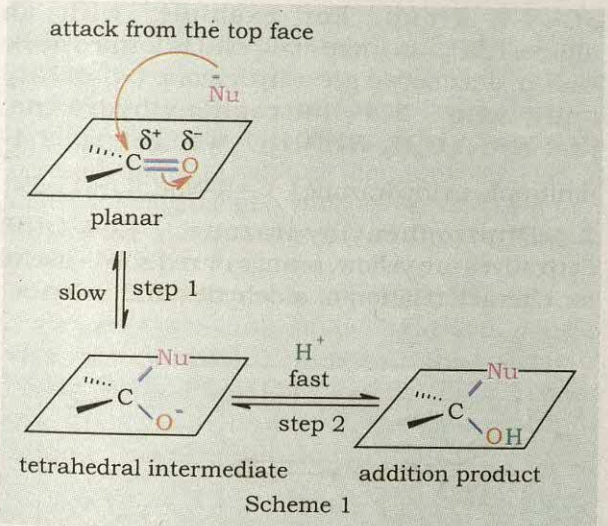
Aldehydes and ketones undergo similar reactions because of the presence of a carbonyl functional group in both of them.

1. Nucleophilic Addition Reactions

Being unsaturated, aldehydes and ketones undergo addition reactions. As seen earlier, the carbon of the carbonyl group is electrophilic, and therefore, susceptible to attack by nucleophiles. Hence, the most typical reactions of aldehydes and ketones are nucleophilic addition reactions to carbon-oxygen double bond.

(i) Mechanism of nucleophilic addition: The attack by the nucleophile (Nu^-) on the carbonyl carbon may occur from above or below the plane of the carbonyl group leading to a C-Nu bond formation. This is accompanied by heterolytic

cleavage of the weaker carbon-oxygen pi-bond with complete transfer of the electron pair of the pi-bond to the oxygen atom. The oxygen atom, thus, gets a negative charge and holds it easily due to its high electronegativity. During this process, the hybridisation of the carbonyl carbon changes from trigonal to tetrahedral and the oxygen atom is pushed out of the plane of the carbonyl group. The negatively charged tetrahedral intermediate is basic and captures a proton from the medium to give the electrically neutral product. The net result is addition of Nu^- and H^+ across the carbon-oxygen double bond (Scheme 1).



Scheme 1

(ii) Reactivity: Aldehydes are more reactive than ketones in nucleophilic addition reactions. This can be understood in terms of the electronic and steric effects. The first step in the above scheme is accelerated by electron withdrawing groups and retarded by electron donating groups. In an aldehyde there is only one electron donating group as against two in ketones. Therefore, aldehydes react faster than ketones. Further, the tetrahedral intermediate is more crowded when bulkier groups are attached to carbonyl carbon. Hence, aldehydes with only one alkyl group and a hydrogen as against two alkyl/aryl groups in ketones will react faster.

Example 14.4

Arrange the following carbonyl compounds in increasing order of their reactivity in nucleophilic addition reactions.

(a) Ethanal, Propanal, Propanone, Butanone.

(b) Benzaldehyde, p-Tolualdehyde, p-Nitrobenzaldehyde, Acetophenone.

Solution

(a) The electron-releasing inductive effect as well as steric crowding increases in the given order. Therefore, the reactivity in nucleophilic addition reactions decreases in this order. Thus, the required order is as follows:

Butanone < Propanone < Propanal < Ethanal.

(b) Acetophenone is a ketone. All the other three compounds are aldehydes. Therefore, acetophenone is the least reactive. p-Tolualdehyde has an electron-donating methyl group at the *para* position of the benzene ring whereas p-nitrobenzaldehyde has an electron-withdrawing nitro group at the para position. Therefore, p-tolualdehyde is less reactive and p-nitrobenzaldehyde is more reactive than benzaldehyde. Hence, the required order is as follows:

Acetophenone < p-Tolualdehyde < Benzaldehyde < p-Nitrobenzaldehyde

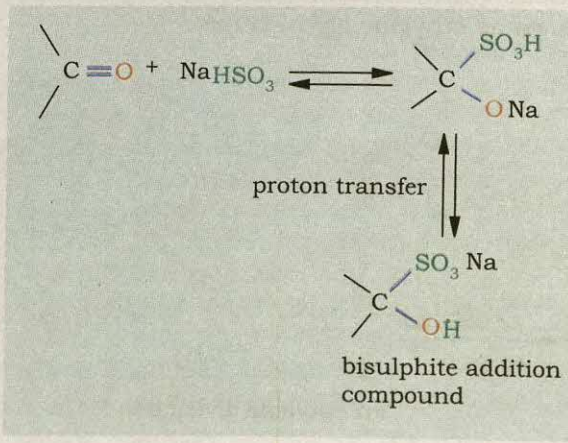
(iii) Some important examples of nucleophilic addition reactions

(a) *Addition of hydrogen cyanide* (HCN): Hydrogen cyanide adds to aldehydes and ketones to form cyanohydrins.

a cyanohydrin

Cyanohydrins are useful synthetic intermediates.

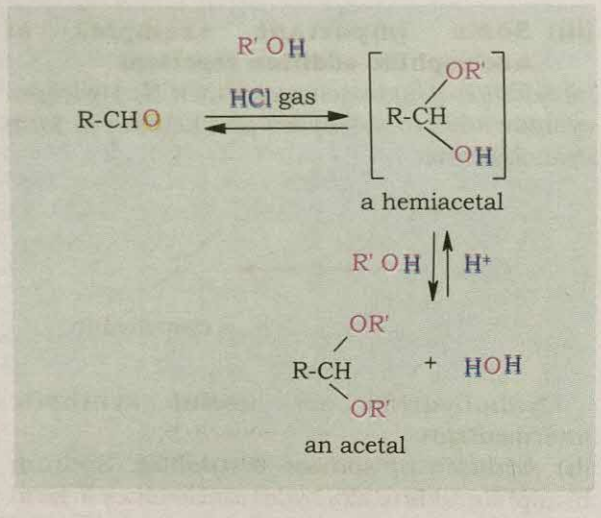
(b) *Addition of sodium bisulphite*: Sodium bisulphite adds to aldehydes and ketones to form crystalline addition products.



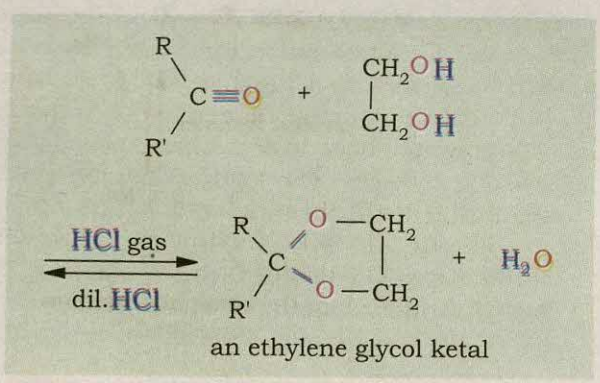
The position of the equilibrium lies largely to the right for most aldehydes and to the left for most ketones. The bisulphite addition compound can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali. Therefore, the bisulphite addition compounds are useful for separation and purification of aldehydes.

(c) *Addition of Grignard reagents*: See Unit 13.

(d) *Addition of alcohols*: Aldehydes react with two equivalents of monohydric alcohols in the presence of dry hydrogen chloride to form *gem*-dialkoxy compounds, known as acetals. Initially, an alkoxyalcohol intermediate, known as hemiacetal, is formed by nucleophilic addition of the alcohol to the carbonyl group. Hemiacetal is unstable in the presence of an acid and reacts with one more equivalent of alcohol to give the acetal.

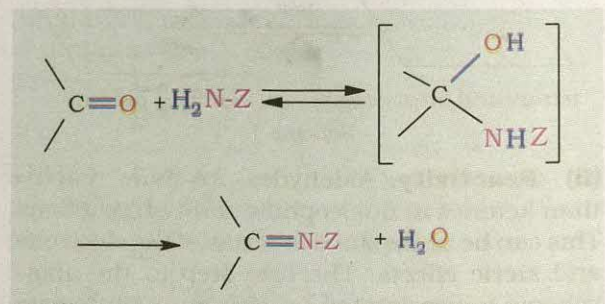


Ketones react with ethylene glycol under similar conditions to form cyclic products, known as ethylene glycol ketals.



Dry hydrogen chloride absorbs the water produced in these reactions and drives the equilibrium in the forward direction. Acetals and ketals are hydrolysed with aqueous mineral acids.

(e) *Addition of ammonia and its derivatives*: Nitrogen nucleophiles, such as ammonia and its derivatives H_2N-Z add to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalysed by acid. The equilibrium favours the product formation due to rapid dehydration of the tetrahedral addition product. The net result is replacement of the >C=O group with >C=N–Z group. For example, with an amine, RNH_2, an imine (>C=NR) is formed while with hydrazine we get a hydrazone (>C=N-NH_2) and with 2,4-dinitrophenylhydrazine, [2,4-$(NO_2)_2C_6H_3$-$NHNH_2$], we get a 2,4-dinitrophenylhydrazone [$\rangle$C=N–$NHC_6H_3(NO_2)_2$-2,4]. 2,4-Dinitrophenylhydrazone, (2,4-DNP) derivatives are yellow, orange or red solids useful for characterisation of aldehydes and ketones.

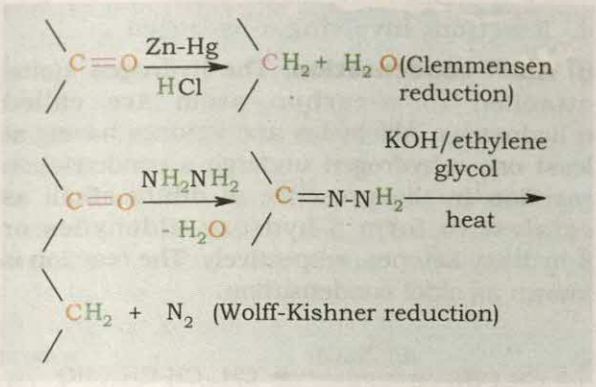


Z=Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$, etc.

2. Reduction

(i) Reduction to alcohols: Aldehydes and ketones are reduced to primary and secondary alcohols, respectively, by complex metal hydrides such as sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$) as well as by catalytic hydrogenation (Unit 13).

(ii) Reduction to hydrocarbons: The carbonyl group of aldehydes and ketons is reduced to CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid (**Clemmensen reduction**) or with hydrazine followed by heating with potassium hydroxide in high boiling solvent ethylene glycol (**Wolff-Kishner reduction**).



3. Oxidation

Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, such as Ag^+ and Cu^{2+} ions can oxidise aldehydes under alkaline conditions.

$$R-CHO \xrightarrow{[O]} R-COOH$$

Ketones are not easily oxidised. Under vigorous condition, their oxidation involves carbon-carbon bond cleavage giving a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.

$$R\text{-}\overset{1}{C}H_2\text{-}\overset{2}{\underset{\underset{O}{\|}}{C}}\text{-}\overset{3}{C}H_2\text{-}R' \xrightarrow{[O]} (R\text{-}COOH + R'\text{-}CH_2COOH)$$

by cleavage of C_1-C_2 bond

+

$(R\text{-}CH_2COOH + R'\text{-}COOH)$

by cleavage of C_2-C_3 bond

The oxidation reaction can thus be used to distinguish aldehydes from ketones.

Distinction between aldehydes and ketones: The following tests are useful for this purpose. Ketones do not respond to these tests.

(i) Tollens' test: On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent) in a clean test tube in a water bath, a bright silver mirror is produced due to the deposition of silver metal on the sides of the test tube. The reaction occurs in alkaline medium.

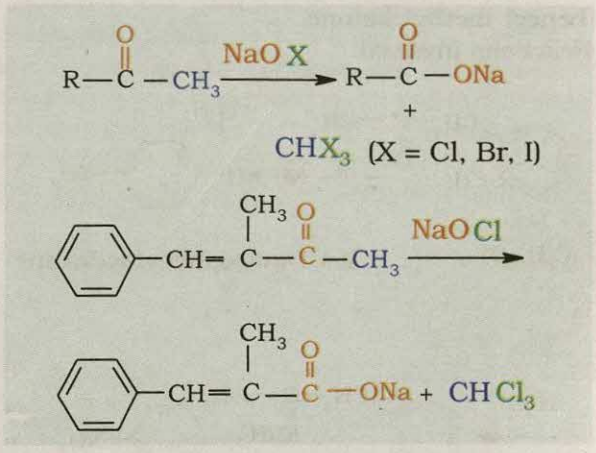
$$RCHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow RCOO^- + 2\,Ag + 2\,H_2O + 4\,NH_3$$

(ii) Fehling's test: On heating an aldehyde with Fehling's solution, [alkaline solution of copper sulphate containing sodium potassium tartarate (*Roschelle salt*)], a reddish brown precipitate of cuprous oxide is formed as a result of the redox reaction. Aromatic aldehydes give very poor results in this test.

$$RCHO + 2Cu^{2+} + 5\,OH^- \longrightarrow RCOO^- + Cu_2O + 3\,H_2O$$

Brown

Oxidation of methyl ketone by haloform reaction: Ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salts of carboxylic acids with one carbon atom less than that of the ketones. The methyl group is converted to haloform(Class XI, Unit 17). This oxidation does not affect a cabon-carbon double bond, if present in the molecule.



Iodoform reaction with sodium hypoiodite can be used for detection of methyl ketones.

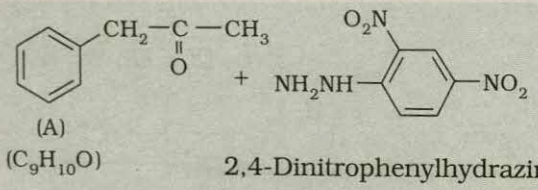
Example 14.5

An organic compound (A) with molecular formula $C_9H_{10}O$ forms orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It does not reduce Tollens' reagent or Fehling solution, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula $C_7H_6O_2$. Identify the compounds (A) and (B) and explain the reactions involved.

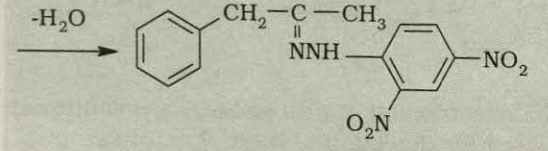
Solution

(A) forms 2,4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollens' reagent or Fehling solution, (A) must be a ketone. (A) responds to iodoform test. Therefore, it should be a methyl ketone. The molecular formula of (A) indicates high degree of unsaturation, yet it does not decolourise bromine water or Baeyer's reagent. This indicates the presence of unsaturation due to an aromatic ring. Compound (B), being an oxidation product of a ketone, should be a carboxylic acid. The molecular formula of (B) indicates that it should be benzoic acid and compound (A) should, therefore, be a monosubstituted aromatic methyl ketone. The molecular formula of (A) indicates that it should be benzyl methyl ketone.

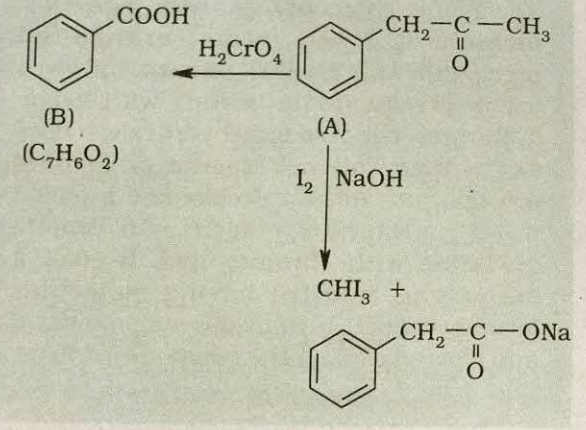
Reactions involved:



(A) $(C_9H_{10}O)$ 2,4-Dinitrophenylhydrazine

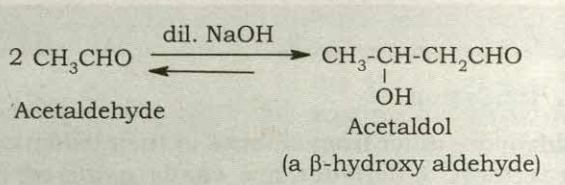


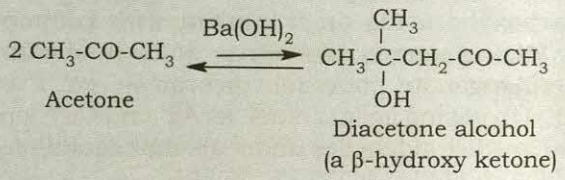
2,4-DNP derivative



4. Reactions involving α-hydrogen

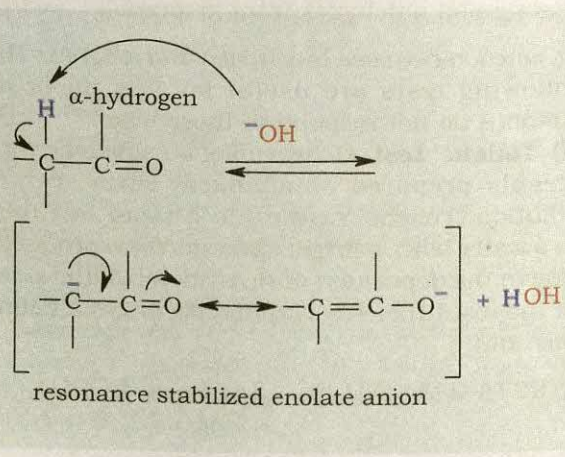
(i) Aldol condensation: The hydrogen atoms attached to α-carbon atom are called α-hydrogens. Aldehydes and ketones having at least one α-hydrogen undergo a condensation reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes or β-hydroxy ketones, respectively. The reaction is known as aldol condensation.





The name aldol condensation is derived from the names of the two functional groups, aldehyde and alcohol, present in the products obtained from aldehydes. Though ketones give ketols (compounds containing a keto and alcohol groups), the general name aldol condensation still applies to the reactions of ketones due to their similarity with that of aldehydes.

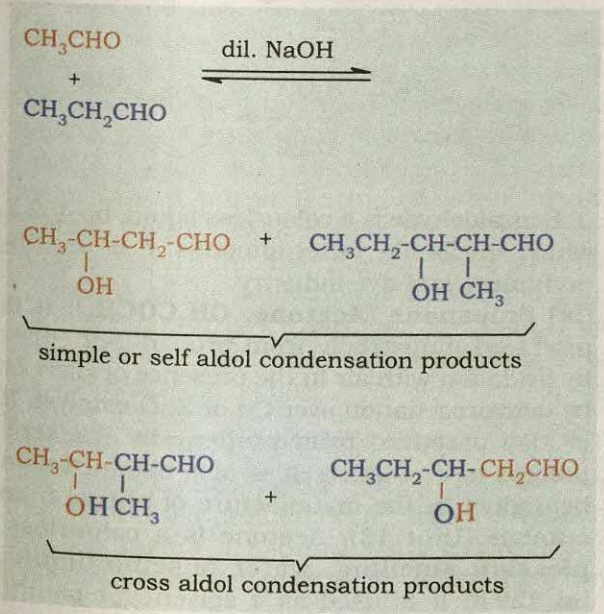
Mechanism: (a) *Acidity of α-hydrogen*: The α hydrogen in aldehydes and ketones is somewhat acidic and may be abstracted by a base, such as NaOH. The acidity of α-hydrogen is due to resonance stabilisation of the conjugate base. The conjugate base is called



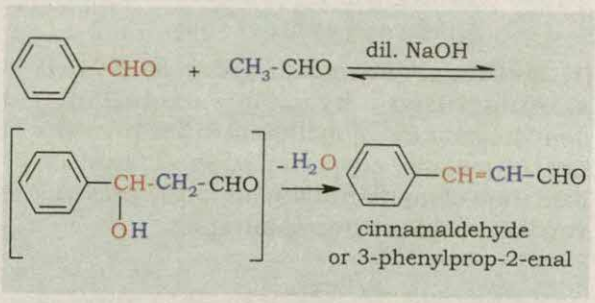
enolate anion after the suffixes for the carbon-carbon double bond (ene) and the alcoholate group present. However, the α-hydrogen is only weakly acidic and the equilibrium of the above reaction lies largely to the left in the presence of a dilute base.

(b) *Nucleophilic addition of enolate anion*: The α-carbon of the enolate anion has considerable negative character and is thus, nucleophilic. It adds to the carbonyl group of the unreacted aldehyde or ketone as usual to give the aldol product.

(ii) Cross aldol condensation: Aldol condensation of a mixture of two different aldehydes or/and ketones, each containing an α-hydrogen, gives a mixture of four products. In this reaction each carbonyl compound produces the corresponding enolate anion, which adds on the carbonyl group of both the carbonyl compounds. Two of the products are thus made up of two molecules of the same carbonyl compound and are known as *self* or *simple aldol condensation products*. The other two products arise from the reaction between one molecule each of the two different carbonyl compounds. These are called *cross aldol condensation products* and the reaction leading to the formation of these products is known as **cross aldol condensation**. This is illustrated below by aldol condensation of a mixture of ethanal and propanal.

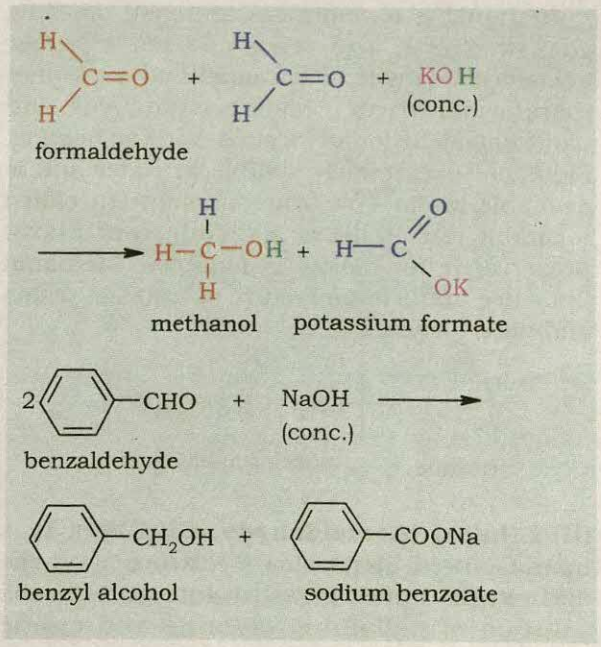


As such, cross aldol condensation is not of much synthetic value. But if one of the carbonyl compounds has no α-hydrogen then it can be of synthetic use. For example, in the reaction between benzaldehyde and acetaldehyde, the cross aldol product is easily formed and loses water molecule to give cinnamaldehyde.



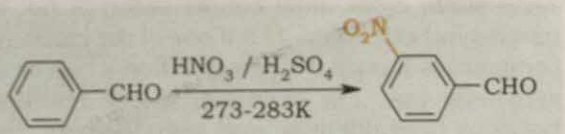
5. Cannizzaro Reaction

Aldehydes, which do not have an α-hydrogen atom, undergo self oxidation and reduction (or disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol and another is oxidised to carboxylic acid salt.



6. Substitution

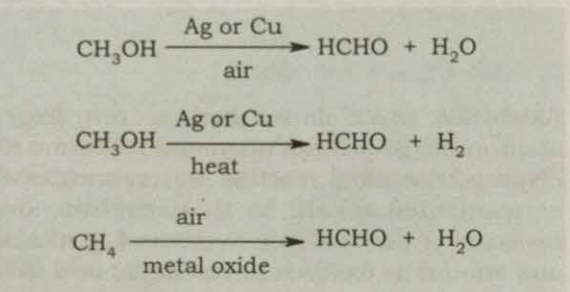
Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and meta-directing group.



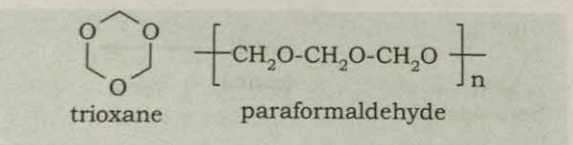
m-nitrobenzaldehyde

14.1.6 Some Commercially Important Aldehydes and Ketones

(i) Methanal (Formaldehyde, HCHO): It is manufactured by air oxidation or dehydrogenation of methanol in the presence of heated metallic copper or silver catalyst or by oxidation of methane with air in the presence of various metallic oxide catalysts.

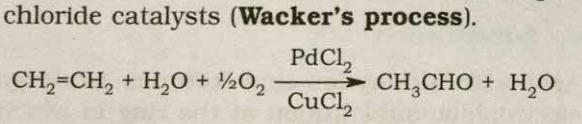


Methanal is a colourless, pungent smelling gas, bp 252 K and readily forms a trimer (metaformaldehyde or trioxane) and a polymer (paraformaldehyde). Metaformaldehyde and paraformaldehyde give formaldehyde on heating. Methanal is extremely soluble in water and is available as its 40% aqueous solution called formalin. Formalin is a disinfectant and a preservative for biological samples. Methanal finds use in the manufacture of bakelite, resins and other polymers.



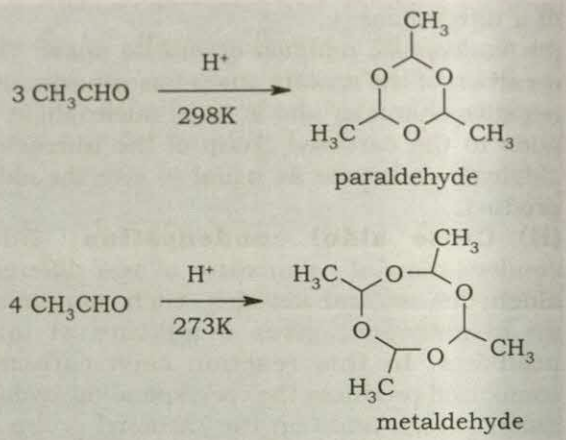
trioxane paraformaldehyde

(ii) Ethanal (Acetaldehyde, CH_3CHO): It is manufactured by passing a mixture of ethene and oxygen under pressure into an aqueous solution of palladium chloride and cupric chloride catalysts (**Wacker's process**).



Wacker's process has almost replaced the earlier method involving hydration of ethyne.

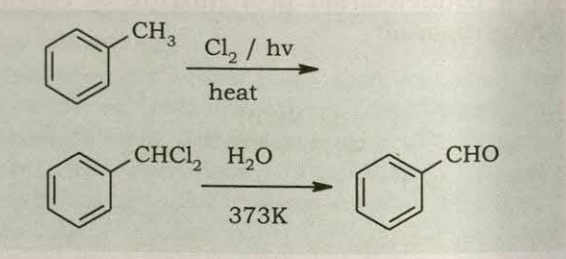
Ethanal is a colourless, pungent smelling, water miscible, volatile liquid, bp 294 K. It forms a trimer (paraldehyde and a tetramer (metaldehyde).



Paraldehyde is a pleasant smelling liquid bp 401K. It is used as a hypnotic. Metaldehyde is a white solid mp 519 K. Both paraldehyde and metaldehyde generate ethanal on distillation with dilute H_2SO_4.

Acetaldehyde is used in the manufacture of acetic acid, ethyl acetate, vinyl acetate, etc.

(iii) Benzaldehyde (C_6H_5CHO): It is obtained commercially by side chain chlorination of toluene followed by hydrolysis.



Benzaldehyde is a colourless liquid, bp 452 K which smells like bitter almonds. It is used in perfumery and dye industry.

(iv) Propanone (Acetone, CH_3COCH_3): It is produced industrially from propan-2-ol either by oxidation with air in the presence of silver or by dehydrogenation over Cu or ZnO catalyst. It is also prepared from propene by Wacker's process (see ethanal). It is also obtained as a byproduct in the manufacture of phenol from cumene (Unit 13). Acetone is a colourless, pleasant smelling, water miscible liquid, bp 329 K. It is used as a solvent for paints,

lacquers, cellulose acetate, etc. It is also used in organic synthesis.

14.2 CARBOXYLIC ACIDS

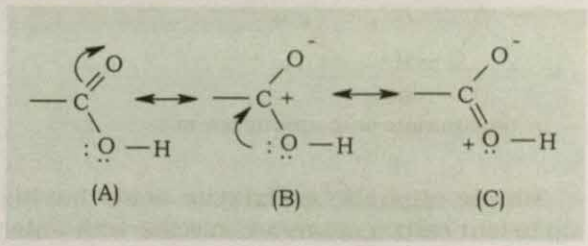
Carbon compounds containing a carboxyl functional group -COOH, are called carboxylic acids. The carboxyl group consists of a *carbonyl* group attached to a hydr*oxyl* group, hence its name *carboxyl*. Carboxylic acids may be aliphatic (RCOOH) or aromatic (ArCOOH) depending on the group, alkyl or aryl, attached to the carboxyl group. Carboxylic acids occupy a central place amongst compounds containing a carbonyl group. A great number of carboxylic acids are found in nature. Some higher members of aliphatic carboxylic acids (C_{12} - C_{18}) occur in natural fats as esters of glycerol. Therefore, these are known as **fatty acids**. Carboxylic acids are not only important as such, but they also serve as starting materials for preparing several other important compounds such as esters, acid chlorides and amides.

14.2.1 Nomenclature

In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending *-e* in the name of the corresponding alkane with *-oic acid*. In numbering the carbon chain, the carboxyl carbon is given number(1). Since carboxylic acids are amongst the earliest organic compounds to be isolated from nature, a large number of them are known by their common names. The common names end with the suffix *-ic acid* and have been derived from Latin or Greek names of their natural sources. For example, formic acid (HCOOH) was first obtained from red ants (Latin: *formica*, means ant), acetic acid (CH_3COOH) from vinegar (Latin: *acetum*, means vinegar), butyric acid ($CH_3CH_2CH_2COOH$) from rancid butter (Latin: *butyrum*, means butter), caproic acid ($CH_3CH_2CH_2CH_2CH_2COOH$) from goats (Latin: *caper*, means goat), etc. The positions of the substituents are indicated by Greek letters α, β, γ, δ, etc., the α-carbon being the one directly attached to the carboxyl group, β- the next, and so on.

14.2.2 Structure of the Carboxyl Group

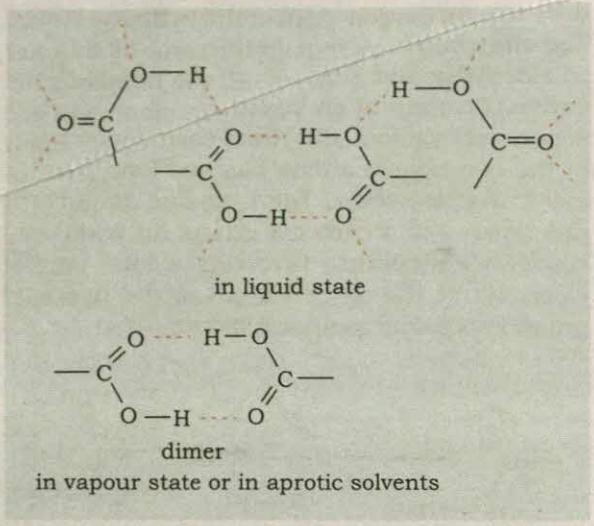
In carboxylic acids one of the two sp^2 hybridised orbitals of the carbonyl carbon, which forms a σ-bond with hydrogen or alkyl(aryl) group in aldehydes and ketones, here does so with oxygen atom of the hydroxyl group. The other bondings remain the same as they are in aldehydes and ketones. All the bonds to the carboxyl carbon atom lie on one plane and are separated by about 120° from each other. Each of the two oxygen atoms has two lone pairs of electrons. However, there is one important difference. For a carboxyl group, an additional resonance structure involving a lone pair of electrons at the oxygen atom of the hydroxyl group is possible as shown below:



The third resonance structure (C) has all atoms with their full quota of electrons (closed shell structure) and thus, is more stable and more important contributor to the resonance hybrid than the second structure (B) in which the positively charged carbon atom has only six electrons in its valence shell (open shell structure). Thus, in two important resonance structures (A) and (C), the carboxyl carbon is electrically neutral. In aldehydes and ketones, only one structrure is electrically neutral. As a result, the carboxyl carbon of the resonance hybrid is less positive and thus, less electrophilic than the carbonyl carbon of aldehydes and ketones. It is clear that carboxyl group is also polar due to resonance structures (B) and (C).

14.2.3 Physical Properties

Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with pungent to unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility. Carboxylic acids are higher boiling than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimers in the vapour phase and in aprotic solvents.



Simple aliphatic carboxylic acids having up to four carbon atoms are miscible with water because they can form hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased influence of the hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic acid, is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, etc.

14.2.4 Methods of Preparation

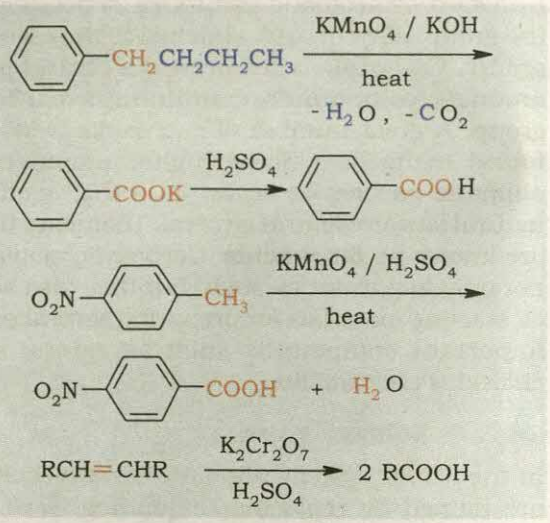
Some important methods of preparation of carboxylic acids are as follows:

1. From primary alcohols and aldehydes: Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate ($KMnO_4$) in neutral, acidic or alkaline media or by potassium dichromate ($K_2Cr_2O_7$) and chromium trioxide (CrO_3) in acidic media. Oxidation with $K_2Cr_2O_7$ or CrO_3 in acidic media often gives some amount of esters. Therefore, oxidation with $KMnO_4$ in neutral or alkaline medium is preferred for the preparation of carboxylic acids. The acid is first obtained as its potassium salt, which on treatment with a mineral acid gives the carboxylic acid. Readily available aldehydes can also be used to obtain carboxylic acids, which may be oxidised even by milder oxidising agents (Section 14.1.4).

$$3\,RCH_2OH + 4\,KMnO_4 \longrightarrow 3\,RCOOK + KOH + 4\,MnO_2 + 4\,H_2O$$

$$2\,RCOOK + H_2SO_4 \longrightarrow 2RCOOH + K_2SO_4$$

2. From alkylbenzenes and alkenes: Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline $KMnO_4$. The entire side chain, irrespective of its length, is oxidised to the carboxyl group. However, if the benzylic carbon is tertiary, oxidation does not occur. Suitably substituted alkenes are also oxidised to carboxylic acids with these oxidising reagents (ClassXI, Unit15).



3. From nitriles: Hydrolysis of nitriles with aqueous acid or alkali gives carboxylic acids (Unit 15).

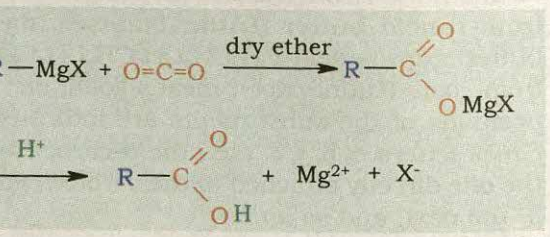
$$R\text{-}C{\equiv}N + 2\,H_2O + H^+ \longrightarrow RCOOH + NH_4^+$$

$$R\text{-}C{\equiv}N + H_2O + {}^-OH \longrightarrow RCOO^- + NH_3$$

$$\downarrow H^+$$

$$RCOOH$$

4. From Grignard reagents: Grignard reagents react with carbon dioxide to form salts of carboxylic acids which give carboxylic acids on acidification with mineral acids.



As Grignard reagents and nitriles are prepared from alkyl halides (Class XI, Unit 17), the above methods are useful for converting an alkyl halide into a carboxylic acid having one carbon atom more than that present in the alkyl halide (ascending the series.)

Example 14.6

Write chemical reactions to effect the following transformations:
(a) Butan-1-ol to Butanoic acid (b) Benzyl alcohol to Phenylethanoic acid (c) Bromobenzene to Benzoic acid (d) p-Methylacetophenone to Benzene-1,4-dicarboxylic acid (e) Cyclohexene to Hexane-1,6-dioic acid.

Solution

(a) $CH_3CH_2CH_2CH_2OH \xrightarrow{\text{aq. } KMnO_4} CH_3CH_2CH_2COOK$
butan-1-ol — potassium butanoate

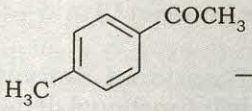
$CH_3CH_2CH_2COOK \xrightarrow{\text{dil. } H_2SO_4} CH_3CH_2CH_2COOH$
butanoic acid

(b) $C_6H_5CH_2OH \xrightarrow{HBr} C_6H_5CH_2Br \xrightarrow{KCN}$
benzyl alcohol — benzyl bromide

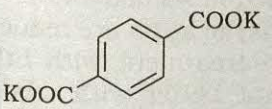
$C_6H_5CH_2CN \xrightarrow{H_3O^+} C_6H_5CH_2COOH$
benzyl cyanide — phenylethanoic acid

(c) $C_6H_5Br \xrightarrow[\text{dry ether}]{Mg} C_6H_5MgBr \xrightarrow{CO_2}$
bromobenzene — phenylmagnesium bromide

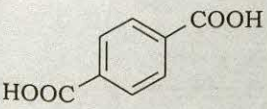
$C_6H_5COOMgBr \xrightarrow{H_3O^+} C_6H_5COOH$
benzoic acid

(d) 

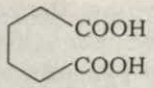
$\xrightarrow{KMnO_4/KOH}$
p-methylacetophenone



$\xrightarrow{\text{dil. } H_2SO_4}$
dipotassium benzene-1,4-dicarboxylate



benzene-1,4-dicarboxylic acid

(e)
$\xrightarrow[H_2SO_4,\ \text{heat}]{KMnO_4}$ 

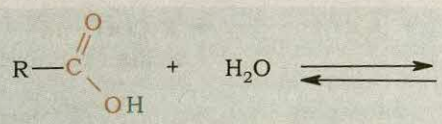
cyclohexene — hexane-1,6-dioic acid

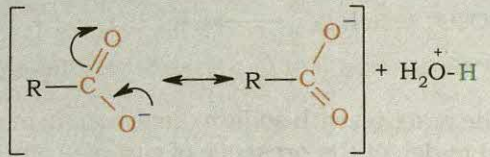
Cyanide route cannot be applied under (c) because bromo group in bromobenzene is not easily replaced by cyano group by reaction of bromobenzene with KCN. Under (d), note that the carbonyl group remains with the benzene ring during oxidation.

14.2.5 Reactions

The reactions of carboxylic acids are mainly due to the carboxyl functional group. You have studied the reactions due to carbonyl group in aldehydes and ketones (Section 14.1.4) and those due to hydroxyl group in alcohols and phenols (Unit 13). Since carboxyl group consists of carbonyl and hydroxyl groups, it is expected to show reactions due to both these groups. However, the reactions expected of these groups are somewhat modified as a result of interaction between these groups due to their close proximity. We have seen in section 14.2.2 that the carbonyl carbon in carboxyl group is less electrophilic than the carbonyl carbon in aldehydes and ketones due to resonance. Therefore, many nucleophilic addition reactions of aldehydes and ketones do not take place with carboxylic acids. The same effect makes the hydroxyl group of carboxylic acids more acidic than the hydroxyl group of alcohols and phenols, justifying why they are called acids. In this section, we shall discuss some reactions of carboxylic acids and return to describe some more later while discussing the reactions of functional derivatives of carboxylic acids.

1. Acidity: In aqueous solution, carboxylic acids dissociate as follows:





resonance stabilised carboxylate anion
equivalent structures

Therefore, they are acidic. However, they are much weaker acids than the mineral acids. The pKa values for most of the simple aliphatic carboxylic acids are of the order of 5, whereas the pKa values for HCl and H_2SO_4 are -7 and -9, respectively. Although weaker than mineral acids, carboxylic acids are stronger acids than alcohols and many simple phenols (pKa is ~16 for ethanol and 10 for phenol). In fact, carboxylic acids are amongst the most acidic organic compounds you have studied so far. You already know why phenols are more acidic than alcohols. The higher acidity of carboxylic acids as compared to phenols can be understood similarly. The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. The conjugate base of phenol, a phenoxide ion, has nonequivalent resonance structures in which the negative charge is at the less electronegative carbon atom. Therefore, resonance in phenoxide ion is not as important as it is in carboxylate ion. Further, the negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion and is less effectively delocalised over only one oxygen and the less electronegative ring carbon atoms in phenoxide ion (Section 13.4.4). Thus, the carboxylate ion derives greater stabilisation on its formation from the carboxylic acid than phenoxide ion does on its formation from phenol. Thus, carboxylic acids are more acidic than phenols.

Accordingly, carboxylic acids not only evolve hydrogen with electropositive metals as alcohols do and form salts and water with alkalis similar to phenols, but also react with weaker bases such as carbonates and bicarbonates to evolve carbon dioxide.

$$R\text{-}COOH + NaOH \longrightarrow R\text{-}COO^- Na^+ + HOH$$

sodium carboxylate

$$R\text{-}COOH + NaHCO_3 \longrightarrow R\text{-}COO^- Na^+ + HOH + CO_2$$

The reaction with sodium bicarbonate may be used to detect the presence of carboxyl group in a compound. Reaction of carboxylic acids with aqueous sodium bicarbonate solution leads to the evolution of carbon dioxide producing effervescence. Most phenols do not produce effervescence with aqueous solution of sodium bicarbonate. Therefore, this reaction may also be used to distinguish between carboxylic acids and phenols.

Effect of substituents on the acidity of carboxylic acids: Substituents may affect the stability of the conjugate base and thus the acidity of the carboxylic acids. Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base. The more powerful and the more the number of such substituents and the closer they are to the carboxyl group, the greater is the inductive effect. Thus, the following orders of acidity can be easily rationalised.

(i) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH > CH_3COOH$

The electronegativity, and thus the electron withdrawing power of the halogen substituent decreases in the given order.

(ii) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$

The number of electron withdrawing chloro group decreases in this order.

(iii) $CH_3CH_2CH(Cl)COOH > CH_3CH(Cl)CH_2\text{-}COOH > ClCH_2CH_2CH_2COOH > CH_3CH_2\text{-}CH_2COOH$

The inductive effect decreases rapidly with increasing distance between Cl and – COOH groups.

2. Conversion into functional derivatives: Carboxylic acids form their functional derivatives by replacement of the hydroxyl group. These reactions are discussed in section 14.3.

3. Reduction: Carboxylic acids are reduced to primary alcohols on treatment with lithium aluminium hydride or better with diborane. Diborane does not easily reduce functional groups such as ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.

$$R-COOH \xrightarrow[\text{or } B_2H_6]{\text{i) } LiAlH_4 \text{ / ether}} R-CH_2OH$$

$$\text{ii) } H_3O^+$$

4. Decarboxylation: Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with soda lime (NaOH + CaO). The reaction is known as decarboxylation.

$$R\text{-}COONa + NaOH \xrightarrow[heat]{CaO} R\text{-}H + Na_2CO_3$$

Alkali metal salts of carboxylic acids undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid. The reaction is known as **Kolbe electrolysis** (Class XI, Unit 15).

5. Substitution in the Hydrocarbon part

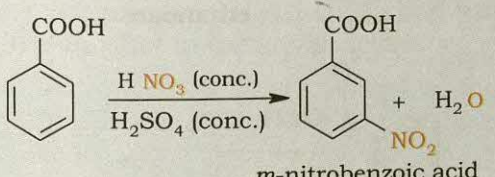
(i) Halogenation: Carboxylic acids having an α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids. The reaction is known as **Hell-Volhard-Zelinsky reaction**.

$$R\text{-}CH_2\text{-}COOH \xrightarrow[ii)\ H_2O]{i)\ X_2 / Red\ P_4}$$

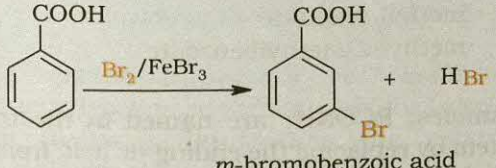
$$R\text{-}\underset{\underset{X}{|}}{C}H\text{-}COOH \qquad (X = Cl, Br)$$

α-halocarboxylic acid

(ii) Ring substitution in aromatic acids: Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group is a deactivating and meta-directing group. Aromatic carboxylic acids, however, do not undergo Friedel-Crafts reaction.



m-nitrobenzoic acid



m-bromobenzoic acid

14.2.6 Some Commercially Important Carboxylic acids

(i) Methanoic acid (Formic acid, HCOOH): It occurs in a variety of biting and stinging plants and insects. It is manufactured by the reaction of carbon monoxide with sodium hydroxide under pressure at 473 K. The resultant sodium methanoate is acidified and distilled to give the acid.

$$NaOH + CO \xrightarrow[10\ atm]{473K} HCOONa$$

sodium methanoate

$$\xrightarrow{H^+} HCOOH$$

methanoic acid

Methanoic acid is a colourless, pungent smelling liquid with bp 373.5 K. Due to the presence of aldehyde-like hydrogen, it is a powerful reducing agent. It reduces Tollens' reagent and Fehling solution. It is used in rubber, textile, dyeing, leather and electroplating industries.

(ii) Ethanoic acid (Acetic acid, CH_3COOH): It is the main constituent of vinegar and is obtained by fermentation of molasses in the presence of air. Industrially, however, it is obtained in pure form by oxidation of ethanal with air in the presence of cobalt acetate catalyst or by carbonylation of methanol in the presence of rhodium catalyst.

$$CH_3CHO + \tfrac{1}{2}O_2 \xrightarrow[353K]{\text{cobalt acetate}} CH_3COOH$$

$$CH_3OH + CO \xrightarrow{\text{Rh catalyst}} CH_3COOH$$

Ethanoic acid is a colourless liquid with pungent odour, bp 391 K. It freezes at unusually high temperature (mp 289 K) forming ice like crystals. For this reason, water free ethanoic acid, obtained by melting of the crystals is called *glacial acetic acid*. It is used in the manufacture of rayon, and in plastic, rubber and silk industries. It is also used as a solvent. Vinegar is used in food industry.

Benzoic acid and 1,2-and 1,4-benzenedicarboxylic acids are obtained by oxidation of toluene and 1,2- and 1,4-dimethylbenzenes, respectively, in air in the presence of various catalysts. These are colourless solids. Esters of benzoic acid are used in perfumery. Sodium benzoate is used as a food

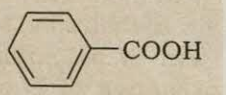
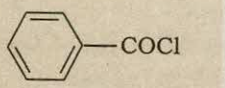
preservative. 1,2-Benzenedicarboxylic acid (phthalic acid) is used in the manufacture of plasticizers and resins. 1,4-Benzenedicarboxylic acid (terephthalic acid) is a basic raw material for polyester.

14.3 FUNCTIONAL DERIVATIVES OF CARBOXYLIC ACIDS

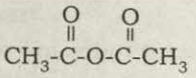
Replacement of hydroxyl group in carboxylic acids with a halogen, carboxylate, alkoxy or amino group gives functional derivatives of carboxylic acids known as acyl halides, acid anhydrides, esters or amides, respectively. The chemistry of these classes of compounds is discussed in this section.

14.3.1 Nomenclature

Acyl halides, R-COX , (sometimes also called acid halides), are named by identifying the acyl group (RCO) and then the halide. The name of the acyl group is derived from the name of the corresponding carboxylic acid by replacing the ending -ic acid by -yl or carboxylic acid by -carbonyl, for example.

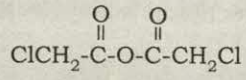
Acid	CH_3COOH	
Common name	Acetic acid	Benzoic acid
IUPAC name	Ethanoic acid	Benzenecarboxylic acid
Acyl halide	CH_3COCl	
Common name	Acetyl chloride	Benzoyl Chloride
IUPAC name	Ethanoyl chloride	Benzenecarbonyl Chloride

Acid anhydrides, RCOOCOR′, are called symmetrical when the two acyl groups are identical, and unsymmetrical when they are different. The names of symmetrical anhydrides of unsubstituted carboxylic acids are derived from the names of the carboxylic acids by replacing the word *acid* with *anhydride*. Symmetrical anhydrides of substituted carboxylic acids are named by adding the prefix bis to the name to indicate that two identical acyl groups are present. Unsymmetrical anhydrides are named by writing the names of the two acids alphabetically before the word anhydride. For example,



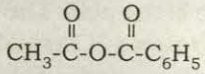
Common name: acetic anhydride

IUPAC name: ethanoic anhydride



bis-(chloracetic) anhydride

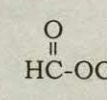
bis-(chloroethanoic) anhydride



acetic benzoic anhydride

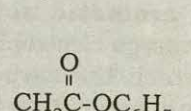
benzoic ethanoic anhydride

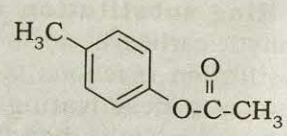
Esters, RCOOR′, are named after the corresponding carboxylic acids by replacing the ending *-ic* acid with *-ate* and preceding this with the name of the *alkyl* or *aryl* group attached to the oxygen atom. For example,



Common name: ethyl formate

IUPAC name: ethyl methanoate



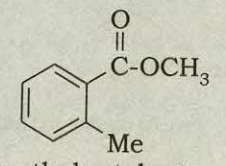


phenyl acetate

p-tolyl acetate

phenyl ethanoate

(4-methylphenyl) ethanoate

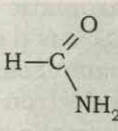


methyl *o*-toluate

methyl 2-methylbenzoate

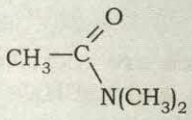
Amides, $RCONH_2$, are named in the trivial system by replacing the ending -ic acid from the name of the corresponding acid with -amide. The

IUPAC names are derived by replacing the ending -oic acid with -amide or carboxylic acid with carboxamide. The position of the substituent at the nitrogen atom, if any, is indicated by the letter N. For example,

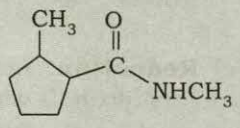


Common name: formamide

IUPAC name: methanamide



N,N-dimethylacetamide



N,N-dimethylethanamide

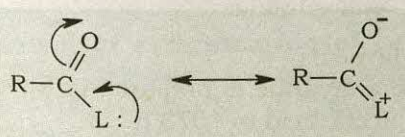
N,2-dimethylcyclopentanecarboxamide

Amides are classified as primary, secondary and tertiary amides depending on whether none, one or two alkyl or aryl groups are attached to the nitrogen atom.

$RCONH_2$	RCONHR′	RCONR′R″
Primary	Secondary	Tertiary

14.3.2 Structures of the Functional Groups Present in Carboxylic Acid Derivatives

The structures of the functional groups present in acyl halide, acid anhydride, ester and amide are similar to that of the carboxyl group we have seen earlier. Due to the presence of lone pairs of electrons at the halogen, oxygen and nitrogen atoms, resonance is possible in these derivatives also, just like that in carboxylic acids.

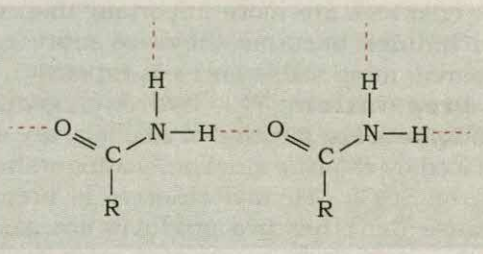


[L = X (halogen), O-COR′, OR′, NH_2]

The relative importance of resonance structures depends on the nature of the L group, which in turn determines the relative electrophilicity of the carbonyl carbon and thus, the relative reactivity of the acyl derivatives. Clearly, all the acid derivatives are polar molecules.

14.3.3 Physical Properties

Being polar in nature, the acid derivatives have higher boiling points than hydrocarbons of comparable molecular masses. Acid chlorides, anhydrides and esters have nearly the same boiling points as the aldehydes and ketones of comparable molecular masses. Their boiling points are however, lower than that of the carboxylic acids of similar molecular masses, apparently due to the absence of hydrogen bonding in acid derivatives. Primary amides have quite high melting points and boiling points because they form strong intermolecular hydrogen bonds, as shown below.



Esters and amides of low molecular masses are fairly soluble in water due to formation of hydrogen bonds with water. The solubility in water decreases with increasing molecular mass and becomes negligible for compounds containing more than six carbon atoms. All the acid derivatives are soluble in usual organic solvents. Volatile esters have pleasant fruity smell. Acyl halides and anhydrides have sharp irritating odours and are lachrymatory (tear producing).

Example14.7

Arrange the following compounds in increasing order of their boiling points: Acetic acid, Methyl formate, Acetamide, Propan-1-ol.

Solution

Methyl formate < Propan-1-ol < Acetic acid < Acetamide

There is no intermolecular hydrogen bonding in methyl formate. Therefore, it is the lowest boiling. Among the remaining three compounds, the intermolecular hydrogen bonding is most extensive in acetamide and least extensive in propan-1-ol. Hence the order.

14.3.4 Reactions and Comparative Reactivity of Acid Derivatives

Most of the reactions of carboxylic acids and their derivatives involve substitution of group L with nucleophiles and are known as *nucleophilic acyl substitution reactions.*

$$RCOL + Nu^- \longrightarrow RCONu + L^-$$

(nucleophilic acyl substitution)

The following order of reactivity of the acid derivatives is observed in the above reaction:

RCOX > RCOOCOR′ > RCOOR′ > $RCONH_2$

acyl halide anhydride ester amide

By nucleophilic acyl substitution reactions, it is possible to interconvert carboxylic acids and their derivatives.

1. Acyl halides

Acyl chlorides are more important than other acyl halides because they are more easily prepared, more stable and less expensive.

(a) Preparation: The hydroxyl group of carboxylic acids, like that of alcohols, are easily replaced by chlorine atom on heating with PCl_5, PCl_3 or $SOCl_2$. Thionyl chloride is preferred because the other two products are gaseous which escape from the reaction mixture. Thus, the purification of the products becomes easier.

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$
$$3RCOOH + PCl_3 \longrightarrow 3\,RCOCl + H_3PO_3$$
$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

Acyl halides cannot be prepared by reaction of carboxylic acids with aqueous halogen acids because they are easily hydrolysed by water.

(b) Reactions: Acyl halides undergo nucleophilic acyl substitution with several nucleophiles. They react with water to give carboxylic acids, with alcohols and phenols to give esters, with ammonia and amines to give amides, and with carboxylate salts to give anhydrides. In these reactions, an acyl group is transferred to the nucleophiles. These reactions are known as **acylation reactions**. Acylation is generally done in the presence of a base in order to neutralise the HX formed. Aliphatic acyl chlorides are very reactive acylating agents. Aromatic acyl chlorides such as benzoyl chloride are less reactive. Benzoyl chloride is hydrolysed only very slowly in water. The acylation of alcohols, phenols and amines by shaking with aromatic acyl chloride in the presence of a base, usually aqueous sodium hydroxide, is known as **Schotten-Bauman reaction**.

The reaction involving cleavage of a bond with alcohol and ammonia such as those mentioned above are known as **alcoholysis** and **ammonolysis**, respectively.

Acid chlorides acylate aromatic hydrocarbons in the presence of anhydrous aluminium chloride to yield aromatic ketones **(Friedel-Crafts acylation)**. *This is a good method for the preparation of aromatic ketones.* The reaction, however, fails when electron withdrawing group is present on the aromatic ring.

$$RCOCl + C_6H_6 \xrightarrow[\text{(anhyd.)}]{AlCl_3} C_6H_5COR + HCl$$

(c) Reduction: Acyl halides are reduced to primary alcohols with $LiAlH_4$ and $NaBH_4$.

$$RCOCl \xrightarrow{LiAlH_4 \text{ (or } NaBH_4)} RCH_2OH$$

Partial reduction of acyl chlorides to aldehydes can also be done by catalytic hydrogenation over palladium catalyst supported on barium sulphate. Generally, small amounts of quinoline (an organic base) and sulphur are added to the reaction which do not allow further reduction to alcohol. The reaction is known as **Rosenmund Reduction**.

$$RCOCl + H_2 \xrightarrow[\text{quinoline sulphur}]{Pd\,/\,BaSO_4} RCHO + HCl$$

2. Acid anhydrides

(a) Preparation: As the name implies, acid anhydrides may be prepared by loss of one molecule of water from two molecules of

$$R{-}\overset{O}{\overset{\|}{C}}{-}OH + HO{-}\overset{O}{\overset{\|}{C}}{-}R \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R + H_2O$$

acid anhydride

carboxylic acids.

Acetic anhydride is prepared industrially by heating acetic acid to 1073 K.

$$2\,CH_3COOH \xrightarrow[\text{porcelain chips, 1073 K}]{\text{quartz tube}} (CH_3CO)_2O + H_2O$$

Acetic anhydride is a dehydrating agent. Higher acid anhydrides can be prepared by heating the acid with acetic anhydride or other

dehydrating agents such as phosphorus pentoxide.

$$2\,RCOOH + (CH_3CO)_2O \xrightarrow{\text{heat}}$$

$$(RCO)_2O + 2\,CH_3COOH$$

$$2\,RCOOH \xrightarrow[\text{heat}]{P_4O_{10}} (RCO)_2O$$

This method is, however, suitable for the preparation of symmetrical anhydrides. As we have seen under acyl halides, symmetrical and unsymmetrical anhydrides may be prepared by the reaction of acyl chlorides with sodium salts of carboxylic acids.

$$RCOCl + R'COONa \longrightarrow RCOOCOR' + NaCl$$

(b) Reactions: Acid anhydrides undergo reactions similar to acyl chlorides. They are also good acylating agents. They are hydrolysed by water. They form esters with alcohols and phenols, amides with ammonia and amines, ketones with aromatic hydrocarbons by Friedel Crafts acylation and primary alcohols with $LiAlH_4$. However, they are less reactive than acyl chlorides and form a carboxylic acid as the byproduct instead of HCl which is a byproduct of acylation with acyl chlorides.

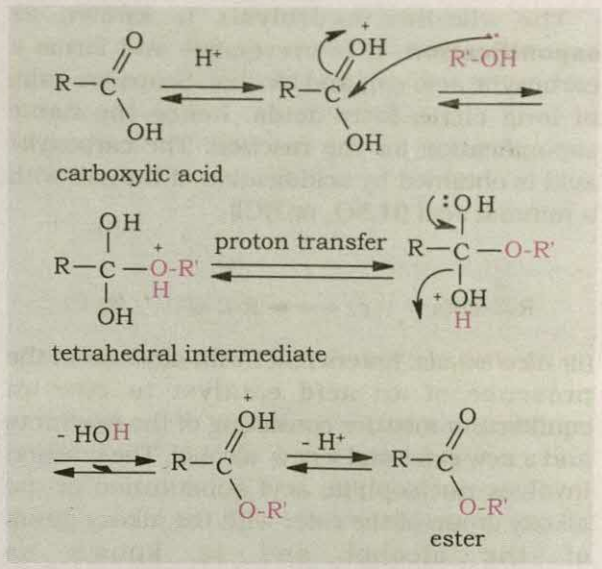
3. Esters

Esters are by far the most important class of acid derivatives.

(a) Preparation: Esters are usually prepared by acylation of alcohols or phenols with carboxylic acids, acyl chlorides or acid anhydrides. The formation of esters is known as **esterification**. You are familiar with esterification of alcohols and phenols with acyl halides and acid anhydrides. Esterification of carboxylic acids with alcohols requires a mineral acid such as concentrated H_2SO_4 or HCl gas as a catalyst **(Fischer esterification)**.

$$RCOOH + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} RCOOR' + H_2O$$

Mechanism of esterification of carboxylic acids: The esterification of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution. Protonation of the carbonyl oxygen activates the carbonyl group towards nucleophilic addition of the alcohol. Proton transfer in the tetrahedral intermediate converts the hydroxyl group into $-\overset{+}{O}H_2$ group, which, being a better leaving group, is eliminated as neutral water molecule. The protonated ester finally looses a proton to give the ester.



The above mechanism is supported by the fact that acetic acid reacted with isotopically labelled methanol ($CH_3{}^{18}\mathbf{O}H$) to give methyl acetate having all the labelled oxygen in the ester while water did not contain any isotopic oxygen.

$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}OH + CH_3{-}{}^{18}OH \underset{}{\overset{H^+}{\rightleftharpoons}}$$

$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}{}^{18}\mathbf{O}\,CH_3 + H_2O$$

All the steps in the above mechanism are reversible. The equilibrium is unfavourable for the preparation of esters of phenols. The nucleophilic attack of phenolic –OH on carbonyl carbon is not favoured due to the electron withdrawing effect of phenyl group. Therefore, such esters are prepared by irreversible acylation of phenols with acyl chlorides or anhydrides.

(b) Reactions: Esters undergo typical nucleophilic acyl substitution reactions but are less reactive than acyl chlorides and anhydrides.

(i) *Hydrolysis*: Esters are hydrolysed by water only slowly to carboxylic acids and alcohols, but the hydrolysis is speeded up in the presence of a mineral acid catalyst or alkali.

$$R{-}\overset{O}{\overset{\|}{C}}{-}OR' + H_2O \text{ (excess)} \underset{}{\overset{H^+}{\rightleftharpoons}} R{-}\overset{O}{\overset{\|}{C}}{-}OH + R'OH$$

$$R{-}\overset{O}{\overset{\|}{C}}{-}OR' + NaOH \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}ONa + R'OH$$

carboxylic acid salt

The alkaline hydrolysis is known as **saponification**. It is irreversible and forms a carboxylic acid salt and alcohol. Soaps are salts of long chain fatty acids, hence the name saponification for the reaction. The carboxylic acid is obtained by acidification of the salt with a mineral acid (H_2SO_4 or HCl).

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}ONa + HCl \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + NaCl$$

(ii) *Alcoholysis*: Esters react with alcohols in the presence of an acid catalyst to give an equilibrium mixture consisting of the reactants and a new ester and a new alcohol. The reaction involves nucleophilic acyl substitution of the alkoxy group of the ester with the alkoxy group of the alcohol and is known as **transesterification**.

$$R-\overset{O}{\overset{\|}{C}}(OR') + R''OH \overset{H^+}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}(OR'') + R'OH$$

Esters also react with ammonia and amines to form amides. Reaction of esters with Grignard reagents gives tertiary alcohols. First a ketone is formed which reacts further with the Grignard reagent to give the tertiary alcohol. The acyl group of an ester is reduced with $LiAlH_4$ (but not with $NaBH_4$) to a primary alcohol. Catalytic hydrogenation of esters to alcohols is not easy unlike that of aldehydes and ketones and requires high temperature and pressure. The catalyst most often used is a mixture of oxides known as copper chromite of approximately the composition $CuO.CuCr_2O_4$. The alkoxy part of the ester gives the corresponding alcohol as by product in all these reactions.

4. Amides

(a) Preparation: Amides are generally prepared by the reaction of acyl chlorides or anhydrides with ammonia or amines. Ammonolysis of esters is also sometimes useful. You have already read about these reactions earlier in this section. Reaction of carboxylic acids with ammonia or amines gives ammonium or substituted ammonium carboxylates. Carboxylate ion shows little reactivity in nucleophilic acyl substitution. Formation of amides occurs only on heating the ammonium salt at relatively high temperatures. Therefore, this method is not useful for laboratory preparation of amides. However, it is useful in industrial preparation of amides.

$$RCOOH + NH_3 \longrightarrow RCOO^- \overset{+}{N}H_4$$

$$\xrightarrow{\text{heat}} RCONH_2 + H_2O$$

(b) Reactions: Due to resonance in amides, they are amphoteric. They are the least reactive class of acid derivatives in nucleophilic acyl substitution reactions. However, they are hydrolysed by aqueous solutions of mineral acids or alkalis to give carboxylic acids.

$$RCONH_2 + H_2O \xrightarrow{H_2SO_4} RCOOH + NH_4HSO_4$$

$$RCONH_2 + NaOH \xrightarrow{H_2O} RCOONa + NH_3$$

Primary amides are dehydrated with phosphorus pentoxide to give nitriles.

$$RCONH_2 \xrightarrow[\text{heat}]{P_4O_{10}} \underset{\text{nitrile}}{RC\equiv N} + H_2O$$

On treatment with nitrous acid, primary amides give carboxylic acids. Nitrogen is eliminated quantitatively in this reaction. The volume of nitrogen can be measured to determine the amide quantitatively.

$$RCONH_2 + HNO_2 \longrightarrow RCOOH + N_2 + H_2O$$

When primary amides are treated with bromine in the presence of an alkali, a primary amine containing one carbon less than the amide is formed.

$$RCONH_2 + 4\,NaOH + Br_2 \longrightarrow$$

$$\underset{\text{prim. amine}}{RNH_2} + 2\,NaBr + Na_2CO_3 + 2\,H_2O$$

The reaction is known as **Hofmann Bromamide reaction** and is useful to prepare lower homologue from a higher one (descending of series).

Amides are reduced to amines with $LiAlH_4$.

$$RCONH_2 \xrightarrow[\text{ii) } H_3O^+]{\text{i) } LiAlH_4} \underset{\text{amine}}{RCH_2NH_2}$$

Example 14.8
Write chemical reactions to effect the following transformations:
(a) Benzoic acid to Benzyl amine
(b) *p*-Nitrobenzoic acid to *p*-Nitroaniline
(c) Hexanoic acid to Hexanenitrile.

Solution
First convert the carboxylic acid to amide as follows:

$$RCOOH \xrightarrow{SOCl_2} RCOCl \xrightarrow{NH_3} RCONH_2$$

Then treat the amide as follows:

(a) $C_6H_5CONH_2 \xrightarrow[ii)\ H_3O^+]{i)\ LiAlH_4} C_6H_5CH_2NH_2$
benzamide — benzyl amine

(b) $p\text{-}O_2NC_6H_4CONH_2 \xrightarrow[Br_2]{NaOH} p\text{-}O_2NC_6H_4NH_2$
p-nitrobenzamide — *p*-nitroaniline

(c) $CH_3(CH_2)_4CONH_2 \xrightarrow[heat]{P_4O_{10}} CH_3(CH_2)_4C \equiv N$
hexanamide — hexanenitrile

Example 14.9
How will you convert hept-1-ene to
(a) Heptanal (b) Hexanal
(c) Hexanoic acid (d) Heptanoic acid.

(a) $CH_3(CH_2)_4CH=CH_2 \xrightarrow[ii)\ H_2O_2/NaOH]{i)\ B_2H_6/ether}$
hept-1-ene

$CH_3(CH_2)_4CH_2CH_2OH \xrightarrow{PCC/\ CH_2Cl_2} CH_3(CH_2)_5CHO$
heptan-1-ol — heptanal

(b) $CH_3(CH_2)_4CH=CH_2 \xrightarrow[ii)\ Zn/\ H_2O]{i)\ O_3} CH_3(CH_2)_4CHO + HCHO$
hexanal; + HCHO (soluble in water, easily removed)

(c) $CH_3(CH_2)_4CH=CH_2 \xrightarrow[H_2SO_4/\ heat]{KMnO_4} CH_3(CH_2)_4COOH$
hexanoic acid

(d) $CH_3(CH_2)_4CH_2CH_2OH \xrightarrow[KOH]{KMnO_4}$
[as obtained under (a)]

$CH_3(CH_2)_5COOK \xrightarrow{dil.\ H_2SO_4} CH_3(CH_2)_5COOH$
heptanoic acid

SUMMARY

Aldehydes, ketones, carboxylic acids and functional derivatives of carboxylic acids (acyl halides, acid anhydrides, esters and amides) are some important organic compounds containing a carbonyl group. These are highly polar molecules. Therefore, they boil at higher temperatures than the hydrocarbons and weakly polar compounds, such as ethers of comparable molecular masses. The lower members are soluble in water because they can form hydrogen bonds with water. The higher members are insoluble in water but soluble in common organic solvents. Aldehydes are prepared by dehydrogenation or controlled oxidation of primary alcohols and controlled reduction of acyl halides (eg. **Rosenmund reduction**). Aromatic aldehydes may be prepared by oxidation of methylbenzenes with CrO_3 in the presence of acetic anhydride or by hydrolysis of benzylidene dichlorides. Ketones are prepared by oxidation of secondary alcohols and hydration of alkynes. A good method for the preparation of aromatic ketones is the **Friedel Crafts** acylation of aromatic hydrocarbons with acyl chlorides or anhydrides. Both aldehydes and ketones can be prepared by ozonolysis of alkenes. Aldehydes and ketones undergo nucleophilic addition reactions onto the carbonyl group with a number of

nucleophiles such as, HCN, $NaHSO_3$, alcohols (or diols), ammonia derivatives, and **Grignard reagents**. The α-hydrogens in aldehydes and ketones are acidic. Therefore, aldehydes and ketones having at least one α-hydrogen, undergo **aldol condensation** in the presence of a base, such as NaOH to give β-hydroxyaldehydes and β-hydroxyketones, respectively. Aldehydes having no α-hydrogen undergo **Cannizzaro reaction** in the presence of concentrated alkali. Aldehydes and ketones are reduced to alcohols with $NaBH_4$, $LiAlH_4$, or by catalytic hydrogenation. The carbonyl group of aldehydes and ketones can be reduced to a methylene group by **Clemmensen reduction** or **Wolff-Kishner reduction**. Aldehydes are easily oxidised to carboxylic acids by mild oxidising reagents such as, **Tollens' reagent** and **Fehling's solution**. These oxidation reactions are used to distinguish aldehydes from ketones. Carboxylic acids are prepared by oxidation of primary alcohols, aldehydes and alkenes, by hydrolysis of nitriles, and by treatment of Grignard reagents with carbon dioxide. Aromatic carboxylic acids can also be prepared by side-chain oxidation of alkylbenzenes. Though much weaker acids than mineral acids, carboxylic acids are considerably more acidic than alcohols and most simple phenols. Carboxylic acids are reduced to primary alcohols with $LiAlH_4$, or better with diborane in ether solution, converted to their functional derivatives, and undergo α-halogenation with Cl_2 and Br_2 in the presence of red phosphorus (**Hell-Volhard-Zelinski reaction**). Functional derivatives of carboxylic acids undergo nucleophilic acyl substitution with nucleophiles. Their reactivity in nucleophilic acyl substitution decreases in the order: acyl halides > acid anhydrides > esters > amides. All the carboxylic acid derivatives can be converted to the parent carboxylic acids by hydrolysis with water under neutral, acidic or alkaline conditions, and reduced to primary alcohols (amides are reduced to amines) with $LiAlH_4$. Primary amides can be dehydrated to nitriles and rearranged to primary amines by treatment with aqueous solution of bromine and alkali (**Hofmann Bromamide reaction**). Several carbonyl compounds such as, methanal, ethanal, propanone, benzaldehyde, formic acid, acetic acid, benzoic acid, 1,2- and 1,4-benzenedicarboxylic acids, benzoyl chloride, acetic anhydride, etc., are important in industry.

EXERCISES

14.1 Name the following compounds according to IUPAC system of nomenclature:

(a) $CH_3CH(CH_3)CH_2CH_2CHO$
(b) $CH_3CH{=}CHCHO$
(c) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$
(d) $OHCC_6H_4CHO$-*p*
(e) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$
(f) $CH_3COCH_2COCH_3$
(g) $(CH_3)_3CCH_2COOH$
(h) $(CH_3)_2CHCH(CH_3)COCl$
(i) $[(CH_3)_2CHCH_2CO]_2O$
(j) $C_6H_5CH_2CH_2COOCH(CH_3)_2$
(k) *m*-$BrC_6H_4CH_2COOCH_2CH_2CH_3$
(l) $CH_3OOCCH_2CH_2COOCH_3$
(m) $CH_3CH(CH_3)CONH_2$
(n) $CH_3CH(Br)CH_2CONHCH_3$

14.2 Draw the structures of the following compounds.

(a) 3-Methylbutanal
(b) *p*-Methylbenzaldehyde
(c) 4-Chloropentan-2-one
(d) *p,p'*-Dihydroxybenzophenone
(e) *p*-Nitropropiophenone
(f) 4-Methylpent-3-en-2-one
(g) 3-Bromo-4-phenylpentanoic acid
(h) Hex-2-en-4-ynoic acid
(i) 2,4-Dimethylpentanoyl chloride
(j) Formic acetic anhydride
(k) Methyl 1-methylcyclohexanecarboxylate
(l) *N*-Ethyl-N-methylbenzamide
(m) *N*,2-Dimethylpropanamide.

14.3 Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

(a) Methanal (b) 2-Methylpentanal (c) Benzaldehyde (d) Benzophenone (e) Cyclohexanone (f) 1-Phenylpropanone (g) Phenylacetaldehyde (h) Butan-1-ol (i) 2,2-Dimethylbutanal.

14.4 How will you convert acetaldehyde into the following compounds?
(a) Butan-2-one (b) Butane-1,3-diol (c) But-2-enal (d) Butan-1-ol (e) Butanoic acid (f) But-2-enoic acid.

14.5 Write structural formulae and names of the four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde served as nucleophile and which as electrophile.

14.6 An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

14.7 An organic compound (A) (Mol. For. $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). Write possible structures of (A) and give their IUPAC names. Also write equations for the reactions involved.

14.8 *N*,*N*-Diethyl-*m*-toluamide is an active ingredient in many insect-repellent preparations. How will you prepare this compound from *m*-bromotoluene?

14.9 Arrange the following compounds in increasing order of their property as indicated:
(a) Acetaldehyde, Acetone, Di-*tert*-butyl ketone, Methyl *tert*-butyl ketone (reactivity towards HCN)
(b) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)
(c) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)
(d) CH_3COCl, CH_3CONH_2, CH_3COOCH_3, $(CH_3CO)_2O$ (reactivity in hydrolysis).

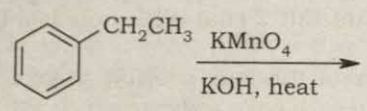
14.10 Give simple chemical tests to distinguish between the following pairs of compounds.
(a) Propanal and Propanone
(b) Phenol and Benzoic acid
(c) Benzamide and *p*-Aminobenzoic acid
(d) Ethanal and Propanal
(e) Methyl acetate and Ethyl acetate
(f) Benzoic acid and Ethyl benzoate
(g) Propanal and Diethyl ether
(h) Propanoyl chloride and Propanoic acid.
(**Hint**: Iodoform test is carried out in hot alkaline medium).

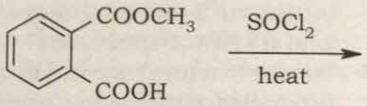
14.11 How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom.
(a) Methyl benzoate (b) *m*-Nitrobenzoic acid (c) *p*-Nitrobenzoic acid (d) Phenylacetic acid (e) *p*-Nitrobenzaldehyde.

14.12 How will you bring about the following conversions in not more than two steps?
(a) Propanone to Propene
(b) Propanal to Butanone
(c) Ethanol to 3-Hydroxybutanal
(d) Benzaldehyde to Benzophenone
(e) Benzaldehyde to 3-Phenylpropan-1-ol
(f) Benzaldehyde to α-Hydroxyphenylacetic acid
(g) Benzoic acid to Benzaldehyde
(h) Propanoyl Chloride to Dipropylamine
(i) Propanoic acid to Propenoic acid
(j) Benzene to *m*-Nitroacetophenone
(k) Bromobenzene to 1-Phenylethanol
(l) Benzoyl chloride to Benzonitrile
(m) Benzoic acid to *m*-Nitrobenzyl alcohol

14.13 Describe the following:
(a) Acetylation
(b) Tansesterification
(c) Cross aldol condensation
(d) Saponification
(e) Cannizzaro reaction
(f) Decarboxylation
(g) Hofmann bromamide reaction.

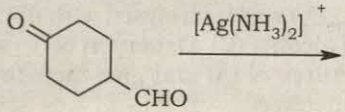
14.14 Predict the organic products of the following reactions:

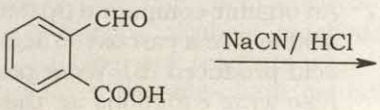
(a) 

(b) 

(c) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

(d) $HCOOCH_3 \xrightarrow[ii)\ H_3O^+]{i)\ CH_3CH_2MgBr\ /\ ether}$

(e) 

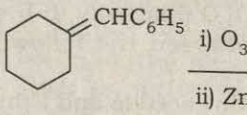
(f) 

(g) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow{\text{dil. NaOH}}$

(h) $CH_3COCH_2COOC_2H_5 \xrightarrow[ii)\ H^+]{i)\ NaBH_4}$

(i) $C_6H_5CON(CH_3)_2 \xrightarrow[ii)\ H_3O^+]{i)\ LiAlH_4,\ ether}$

14.15 Identify compounds (A)-(F) in the following reactions:

(i) 

(A) + (B)

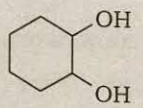
(ii) (E) $\xrightarrow[ii)\ H_2O]{i)\ LiAlH_4/ether}$ (F) + (G)

(A) + (B) $\xrightarrow[\text{aq. ethanol}]{\text{dil. NaOH}}$ (C) + H_2O

(F) $\xrightarrow{PCC/CH_2Cl_2}$ (H)

(C) $\xrightarrow[ii)\ Zn/H_2O]{i)\ O_3}$ (D) + (A)

(H) $\xrightarrow{KOH\ (conc.)}$ (I) + ((F)

(D) $\xrightarrow{H_2/Pt}$ 

(I) $\xrightarrow{(J)}$ $(C_6H_5CO)O$

(G) $\xrightarrow[NaOH]{(J)}$ $C_6H_5COOC_6H_5$

14.16 Give plausible explanation for each of the following:

(a) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.

(b) There are two -NH_2 groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

(c) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as fast as it is formed.

UNIT 15

ORGANIC COMPOUNDS WITH FUNCTIONAL GROUPS CONTAINING NITROGEN

OBJECTIVES

After studying this Unit, you will be able to:

- learn that nitro group in addition to its conversion to other groups influences the reactivity of alkyl or aryl group to which it is attached.
- explain the basic character of amines in relation to their structures.
- learn that unshared pair of electrons and the H present on nitrogen are responsible for reactions of amino groups.
- understand that with organic cyanides and isocyanides, a variety of useful reactions can be performed.
- appreciate the usefulness of aryl diazonium salts in organic synthesis and formation of azo dyes.

"The chief commercial use of amines is as intermediates in the synthesis of dyes, synthetic fibres and medicines."

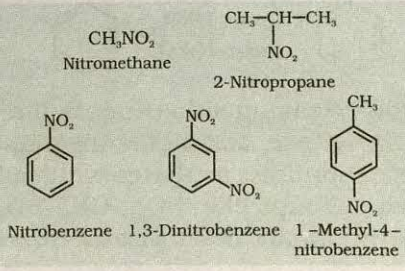
Functional groups containing nitrogen are present in a variety of naturally occurring as well as man made organic compounds. These functional groups impart physicochemical characteristics to these molecules. These groups are responsible for their unique chemical reactivity patterns and play crucial roles in the preparation of drugs, agrochemicals, dyes and molecules of life. There are many functional groups, which contain one or more nitrogen atoms. Some categories of compounds based on these functional groups include nitro compounds, amines, cyanides, isocyanides and diazo compounds. We shall now consider some compounds containing these functional groups.

15.1 NITRO COMPOUNDS

Organic nitro compounds possess nitro (NO_2) functional group. Because of their easy availability, conversion to other functional groups and the influence of the nitro group on the overall reactivity of the molecule, they play a central role in syntheses.

15.1.1 Nomenclature

Nitro compounds are named by putting a prefix nitro to the parent compound. The number and position of nitro groups are also indicated in the prefix as given below:



15.1.2 Methods of Preparation

The methods of syntheses of aromatic and aliphatic nitro compounds are quite different.

1. Aliphatic Nitro Compounds

Two methods used for the preparation of aliphatic nitro compounds are:

(i) Vapour phase nitration of alkanes: Hydrocarbons on heating with fuming nitric acid at 693-793 K are converted into nitroalkanes.

$$CH_3-CH_3 + HNO_3 \xrightarrow{\Delta} CH_3-CH_2-NO_2 + H_2O$$

(Fuming) (low yield)

The nitration of saturated aliphatic hydrocarbons is important commercially for bulk production of low molecular mass nitroalkanes but is of little significance as a laboratory method.

(ii) Treatment of alkyl halides with alcoholic $AgNO_2$: Iodoalkanes on treatment with alcoholic $AgNO_2$ are converted into nitroalkanes besides alkyl nitrites.

$$CH_3-CH_2-I + AgNO_2 \xrightarrow[\text{Alc.}]{} CH_3-CH_2-NO_2$$

Nitroethane

$$+ C_2H_5-O-N=O$$

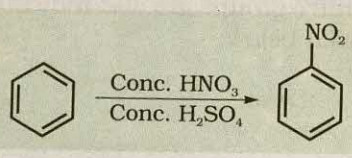
Ethyl nitrite

(iii) Oxidation of t-alkyl amines with $KMnO_4$: Here, the amine must be primary and $-NH_2$ group should be attached to a tertiary carbon.

$$H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-NH_2 \xrightarrow{KMnO_4} H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-NO_2 \quad 83\%\ \text{yield}$$

2. Aromatic Nitro Compounds

For direct nitration of aromatic compounds, the choice of nitrating agent depends upon the reactivity of the aromatic compound. Nitration is performed with a mixture of concentrated nitric and sulphuric acids (Class XI, Unit 15), which is a source of nitronium ion.

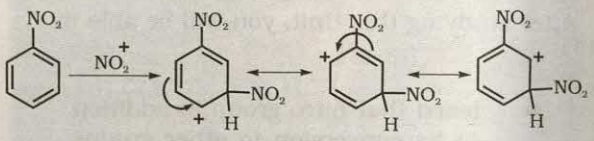


Electron releasing substituents like - CH_3 $-OCH_3$, -OH, $-NH_2$ etc., activate the ring and stabilize the carbocation intermediates while electron withdrawing groups like $-NO_2$, -CN, $-SO_3H$, -X, deactivate the ring and destabilize the carbocation.

This nitrating mixture, nitrates even deactivated aromatics like nitrobenzene under refluxing conditions to give m-dinitrobenzene. For nitration of activated aromatic systems like phenols and their ether derivatives, even milder conditions can be used.

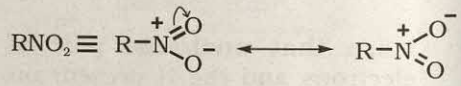
Example 15.1
Write three canonical forms of carbocation intermediate for *m*-attack on nitrobenzene.

Solution:



15.1.3 Electronic Structure and Properties

General structure of a nitro group as represented below is a resonance hybrid of two equivalent zwitterionic, polar structures.



The hybrid structure has a positively charged nitrogen and two equivalent negatively charged oxygens. As a result of the above structural character, the nitro group shows the following physical properties.

The two N-O bonds have equal bond lengths (121 pm in nitromethane) which is intermediate between N-O single bond (136 pm) and N=O double bond (116 pm).

Nitro compounds have large dipole moments amongst simple organic compounds. Due to polarity, their boiling points are unusually high in comparison with other compounds of same molecular mass. Lower members are liquids and higher members are solids. They are soluble in most organic solvents but only lower liquid members have some solubility in water.

Compound	b.p./K	dipole moment/D
Nitromethane	374	3.46
Methane	110	–
Nitrobenzene	484	4.21
Benzene	353.1	–

The formal positive charge on nitrogen of nitro group makes it a strong electron-withdrawing group and exerts a strong pull on neighbouring electrons affecting the physicochemical properties of the molecule. The presence of nitro group in phenols enhances their acidity and in aromatic compounds deactivates them towards electrophilic substitution (Unit 13).

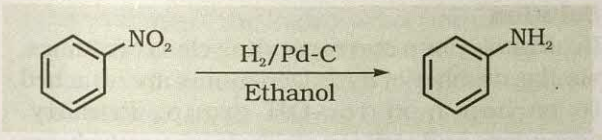
15.1.4 Reactions of Nitro Compounds

In aromatic and aliphatic nitro compounds, nitro group undergoes almost similar reactions, however, the different ways in which it affects the reactivity of the attached aryl or alkyl group are very important in synthesis.

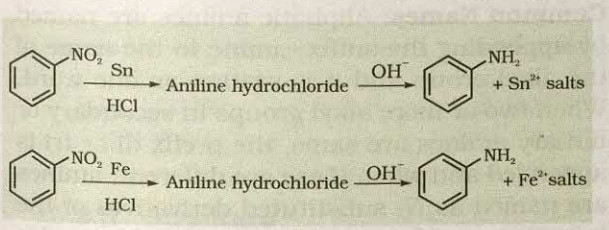
1. Reduction

Nitro compounds can be reduced to primary amines under a variety of conditions.

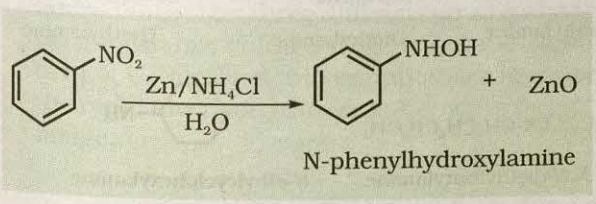
(i) *Catalytic Reduction*: The nitro group is easily reduced by catalytic hydrogenation using Pd/C catalyst in ethanol.



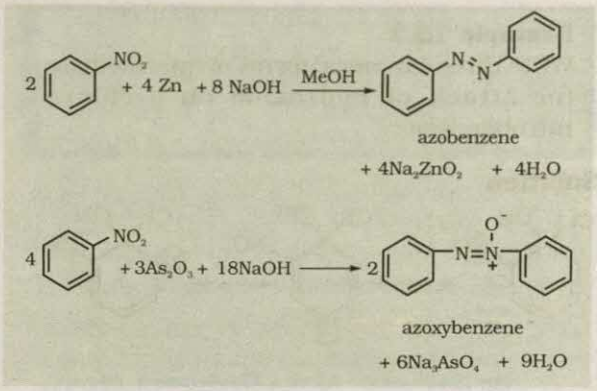
(ii) *Reduction by Metal in Acidic Solutions*: In this method a metal (Fe, Sn or Zn) and HCl are used for reducing a nitro group to an amino group.



(iii) *Reduction in Neutral Medium*: Zinc dust and ammonium chloride convert nitrobenzene to corresponding hydroxylamine.

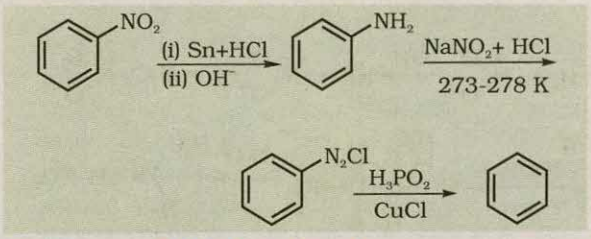


(iv) *Reduction in Alkaline Medium*: Depending upon the nature of the reducing agent, nitrobenzene forms different products as depicted below.



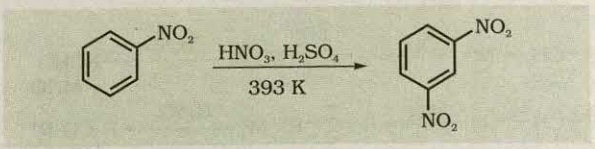
2. Reductive Removal of Nitro Group

The nitro group can be removed from an aromatic ring via reduction to amine followed by diazotisation with HNO_2 and then reductive removal of the diazonium group using sodium borohydride or hypophosphorus acid/Cu^+ mixture.



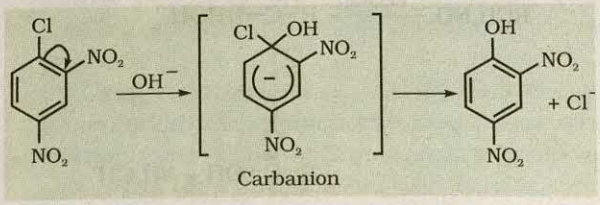
3. Electrophilic Substitution

The nitro group strongly deactivates the benzene ring towards electrophilic substitution. Only under strong conditions of heating with conc. nitric acid and conc. sulphuric acid, nitrobenzene is converted to *m*-dinitrobenzene.



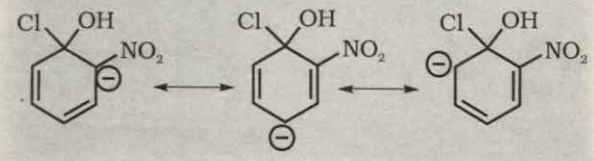
4. Influence on the Reactions of other Functional Groups

The presence of nitro group facilitates nucleophilic substitution of otherwise unreactive aromatic halides by stabilizing the intermediate carbanion as depicted below.



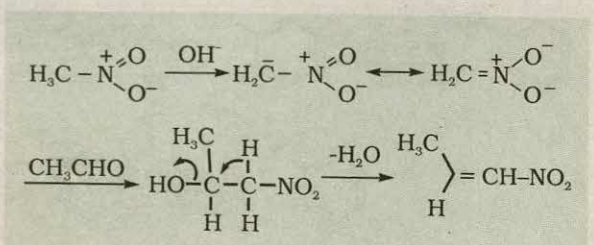
Example 15.2
Write three canonical forms of intermediate for attack of hydroxide on o-chloro nitrobenzene.

Solution



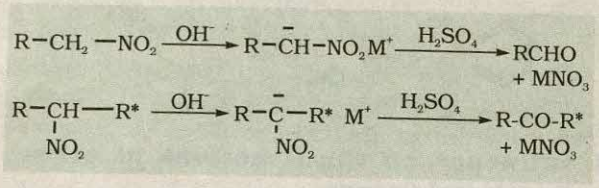
5. Acidic Nature of Alpha Hydrogen Atom

Alpha hydrogen atom in case of aliphatic nitro compounds becomes acidic due to the electron withdrawing nature of nitro group. This nucleophilic anion performs reactions with electrophiles such as acetaldehyde to form aldol condensation product which on dehydration gives unsaturated nitro compound.

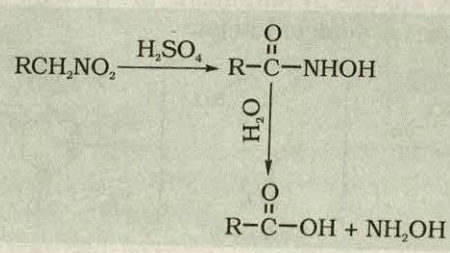


6. Hydrolysis of Aliphatic Nitro Compounds

(i) Primary or secondary aliphatic nitro compounds can be converted to aldehydes or ketones, respectively, by treatment of their carbanion salts with sulphuric acid.



(ii) When primary nitro compounds are treated with H_2SO_4 without prior conversion to salts, they give carboxylic acids.



15.2 AMINES

Amines are organic compounds, which can be structurally derived from ammonia by replacing its one, two or three hydrogens by alkyl and/or aryl groups. Thus, amines have - NH_2, -NH- and >N- functional groups

15.2.1 Classification

Amines, in which two hydrogen atoms are attached to nitrogen are classified as primary amines and those in which one hydrogen atom is attached to nitrogen are called secondary amines. In tertiary amines, the nitrogen atom does not bear any hydrogen and is attached to three alkyl and/or aryl groups.

$(Ar/R)\text{-}NH_2$	$(Ar/R)_2\text{-}NH$	$(Ar/R)_3\text{-}N$
Primary amine	Secondary amine	Tertiary amine

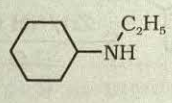
Example 15.3
How is the classification of amines different from that of alcohols?

Solution
In alcohols, for a corresponding class of amines, similar number of hydrogen atoms are attached to carbon next to -OH group. Primary, secondary and tertiary alcohols respectively are RCH_2OH, R_2CHOH, R_3COH

15.2.2 Nomenclature

Common Names: Aliphatic amines are named by appending the suffix -amine to the name of the alkyl group and it is written as one word. When two or more alkyl groups in secondary or tertiary amines are same, the prefix di or tri is appended and when these are different, amines are named as *N*- substituted derivatives of the largest group of primary amine. Some examples are given below.

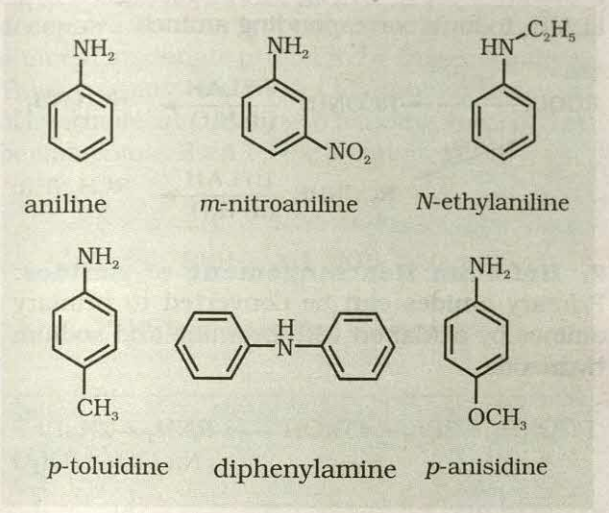
$C_2H_5NH_2$	$(C_2H_5)_2NH$	$(C_2H_5)_3N$
Ethylamine	Diethylamine	Triethylamine



$(C_2H_5)_2N\text{-}CH_2CH_2CH_2CH_3$	
N,N-diethylbutylamine	*N*-ethylcyclohexylamine

Aromatic amines are named as derivatives of the parent member, aniline, but in some cases other names *o/m/p*-toluidine for *o/m/p*-methylaniline and *o/m/p*-anisidine for *o/m/p*-

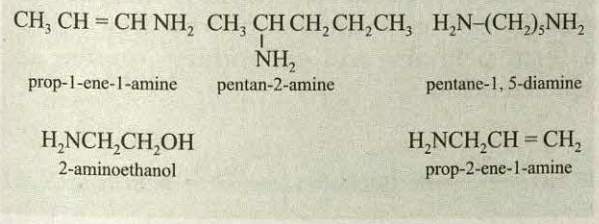
methoxy anilines are assigned. Even *N*-phenyl derivative of aniline is generally called diphenylamine.



aniline | *m*-nitroaniline | *N*-ethylaniline

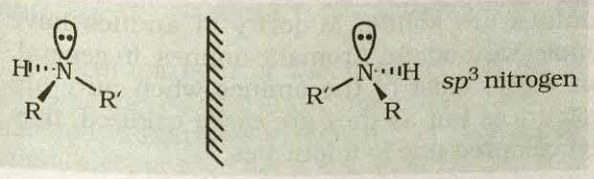
p-toluidine | diphenylamine | *p*-anisidine

IUPAC Names: The ending e of the alkane is replaced by suffix -amine. In case of diamines, the ending e of the hydrocarbon name is retained and suffix diamine is appended. When additional functional groups such as OH or double bond are present in an amine, the prevailing priority order for nomenclature is observed.

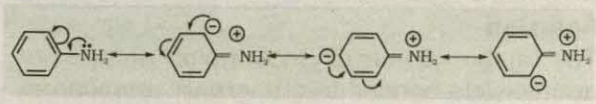


15.2.3 Structure

Aliphatic amines have a pyramidal shape that is approximately tetrahedral when we assume electron pair on nitrogen as a group. Thus, an amine which has three different groups attached to nitrogen has chiral nitrogen. But such amines cannot be resolved into enantiomers because of the rapid inversion of an enantiomer to its mirror image.



In aromatic amines, the electron pair of nitrogen can conjugate with the benzene ring giving carbon nitrogen bond with double bond character. This is why the C-N bond in aromatic amines is shorter than that in aliphatic amines.

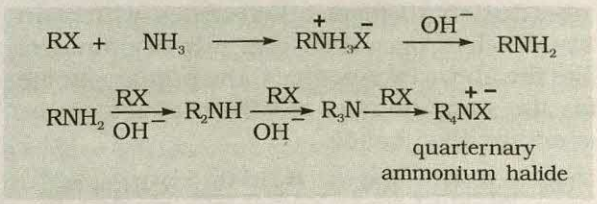


15.2.4 Methods of Preparation

Amines are prepared from a variety of compounds. Some methods commonly used for amines in the laboratory using nitro compounds, alkyl halides, aldehydes and ketones, amides, nitriles and azides are outlined below:

1. Reduction of Nitro Compounds : As outlined earlier (Sec. 15.1.4), nitro compounds are reduced to amines either by catalytic hydrogenation or by using a metal and an acid.

2. Ammonolysis of Alkyl Halides : When an alkyl or a benzyl halide reacts with ammonia, it undergoes nucleophilic substitution and the ammonium salt formed initially, on basification gives a primary amine. Being a nucleophile, the amine can further react with alkyl halide and this sequence of reactions can form secondary and tertiary amines and finally quaternary ammonium salts as depicted below. So, these reactions result in the formation of a mixture of products.



In the ammonolysis of alkyl halides, there are two ways of getting only one product.

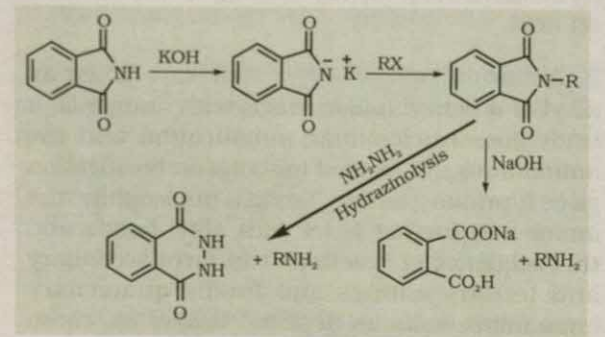
(i) *Using Large Excess of Ammonia*: Under these conditions in the reaction mixture, an alkyl halide is more likely to encounter and react with a molecule of ammonia than with a molecule of amine which is present in relatively much smaller amount and primary amine is the only product.

(ii) *Using a Large Excess of Alkyl Halide*: Under these conditions, in the presence of a base which will consume HX formed, quaternary ammonium salt is the only product.

Example 15.4
Why do quaternary ammonium salts having four different groups attached to nitrogen show optical activity?

Solution
The unshared pair of electrons on nitrogen in amines gets bonded in quaternary ammonium salt with the result that two enantiomers can exist with optical activity.

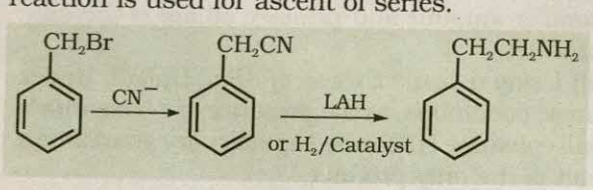
3. Gabriel Synthesis of Primary Amines: Using excess of ammonia in ammonolysis of alkyl halides is not a very practicable method for the synthesis of primary amines. Alternately, a mononucleophilic ammonia derivative; phthalimide is alkylated with alkyl or benzyl halide and then hydrolysed or hydrazinolysed to get pure primary amine.



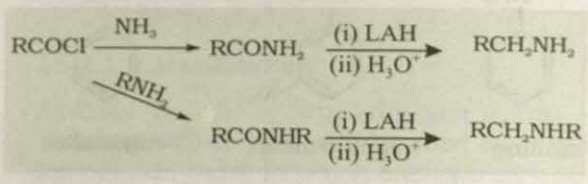
4. Reduction of Azides: On treatment with sodium azide, alkyl halides undergo nucleophilic substitution to form alkyl azides which on catalytic hydrogenation give primary amines. Like the above two methods, the primary amine has the same number of carbon atoms as the precursor alkyl halide.

$$RX \xrightarrow{NaN_3} RN_3 \xrightarrow{H_2/Pd\text{-}C} RNH_2 + N_2$$

5. Reduction of Nitriles: On treatment with sodium cyanide, alkyl halides undergo nucleophilic substitution to form alkyl nitriles which on reduction with $LiAlH_4$(LAH) or catalytic hydrogenation, form primary amines which have one carbon more than the alkyl halide used. This reaction is used for ascent of series.



6. Reduction of Amides: Acyl halides on treatment with ammonia or amines form primary, secondary or tertiary amides which are reduced with a strong reducing agent like $Li AlH_4$ to form corresponding amines.

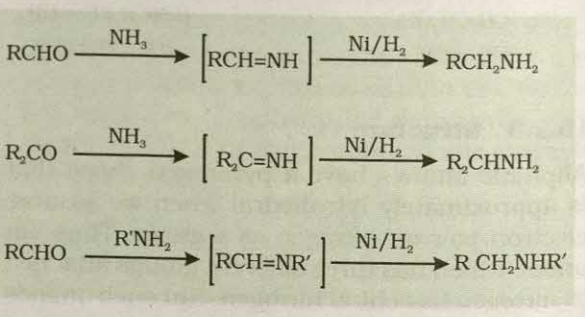


7. Hofmann Rearrangement of Amides: Primary amides can be converted to primary amines by oxidation with bromine and sodium hydroxide.

$$RCONH_2 + 2Br_2 + 4NaOH \longrightarrow RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

This reaction involves migration of alkyl group from carbonyl in the precursor to nitrogen with the elimination of CO_2. Evidently, the reaction provides the product containing one carbon less than the starting material.

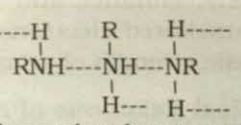
8. Reductive Amination of Carbonyl Compounds: Aldehydes and ketones, on reaction with ammonia or a primary amine form imines which can be reduced on catalytic hydrogenation or using sodium cyanoborohydride ($NaCNBH_3$) to form primary and secondary amines as depicted below.



15.2.5 Physical Properties

Lower members of amines are gases, most of the higher members are liquids while some aromatic amines are solids. Majority of amines have unpleasant odour. Aromatic amines, in general, are toxic. Most of the amines when pure are colourless but as they are easily oxidized, they get coloured due to impurities.

Amines are polar compounds and have higher boiling points than non-polar compounds such as hydrocarbons of the same molecular mass. All amines can form hydrogen bonds as proton acceptors, but only primary and secondary amines can donate proton in hydrogen bonding. Thus, primary and secondary amines, because of intermolecular hydrogen bonding, have higher boiling points than tertiary amines.



Hydrogen bonding in amines

Amine	Molar mass	b.p./K
n-$C_4H_9NH_2$	73	350.8
$(C_2H_5)_2NH$	73	329.3
$C_2H_5N(CH_3)_2$	73	310.5
$C_2H_5CH(CH_3)_2$	72	300.8
n-C_4H_9OH	74	390.3

All the three classes of amines can form hydrogen bonds with water. Amines of low molecular mass are soluble in water but when the hydrophobic part of the amine possess more than six carbons, their solubility in water decreases and still larger amines are essentially insoluble in water. Because of their weaker hydrogen bonds, the solubility of amines in water is less than that of alcohols. Amines are soluble in organic solvents like ether, benzene, alcohol, etc.

15.2.6 Basic Character of Amines

All classes of amines contain nitrogen atoms that bear unshared pair of electrons. The tendency of nitrogen to share these electrons with acids is responsible for the basic character of amines which is affected by the number and the nature of their alkyl or aryl groups.

Like ammonia, amines are strong bases and react with mineral acids to form ammonium salts from which they can be liberated by treatment with a strong base (such as sodium hydroxide).

$$RNH_2 + HCl \longrightarrow RNH_3^+Cl^- \xrightarrow{OH^-} RNH_2 + H_2O + Cl^-$$

For comparison of the basic character of amines, the equilibrium constant of following reaction is taken as a measure of their basic character:

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + \bar{O}H$$

$$K_{eq} = \frac{[RNH_3^+][\bar{O}H]}{[RNH_2][H_2O]}$$

Since $[H_2O]$ is constant, it is convenient to incorporate it into the equilibrium constant, thereby giving the following expression for the basicity constant K_b.

$$K_b = K_{eq}[H_2O] = \frac{[RNH_3^+][\bar{O}H]}{[RNH_2]}$$

All classes of aliphatic amines (K_b of about 10^{-3} to 10^{-4}) are somewhat stronger bases than ammonia (K_b, 1.8×10^{-5}). Aromatic amines are weaker bases ($K_b \sim 10^{-9}$) and substituents on their aromatic ring have a marked affect on their basicity as p-nitroaniline is only 1/4000 as basic as aniline.

Structure -Basicity Relationship of Amines: The basic character of an amine depends on the ease of formation of its ammonium cation by accepting a proton and is thus directly related to the stability of this cation. So, for understanding basic character of amines in relation to their alkyl/aryl groups, we have to compare the stabilities of the amines with the stabilities of the cations they form after protonation.

In aliphatic amines, the electron-releasing alkyl groups stabilise their ammonium cations by dispersing the positive charge, and in parent amine make the nitrogen unshared electrons more available for sharing with a proton. Thus, the basic character of aliphatic amines should increase with increase of alkyl substitution. But it does not occur in a regular manner as a secondary aliphatic amine is unexpectedly more basic than a tertiary amine in solutions.

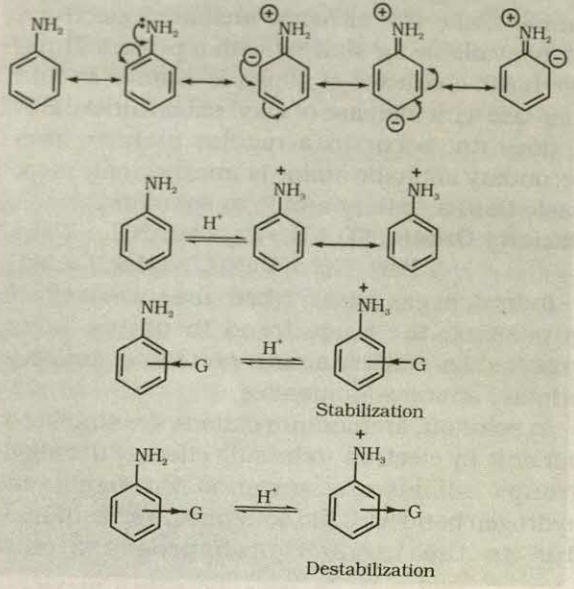
Basicity Order: $(ET)_2NH > Et_2N > EtNH_2 > NH_3$;
$(Me)_2NH > MeNH_2 > (Me)_3N > NH_3$

Indeed, in gas phase, where the solvent effect is missing, the basic trend in nature is as expected i.e. tertiary amine>secondary amine > primary amine > ammonia.

In solution, ammonium cations are stabilized not only by electron -releasing effect of the alkyl groups but also by solvation through their hydrogen bond with the solvent. It is evident that due to the number of hydrogen atoms

present on the nitrogen and thereby similar number of hydrogen bonds, the stability of aliphatic ammonium cations and also the basic strength will be in the order: primary> secondary> tertiary, which is opposite to the alkyl group electron-releasing effect based basic strength order. There could also be some steric repulsion to H-bonding in cations derived from tertiary amines. In view of these considerations, it may be concluded that it is a combination of electron-releasing, H-bonding and steric factors that determine the stability of the ammonium cations in solution and thereby resulting in the basic strength order of aliphatic amines as secondary> tertiary >primary amines.

Aromatic amines are weaker bases than ammonia and aliphatic amines. For a structural explanation of this property, we should realise that an additional feature in the structures of aromatic systems is their resonance stabilization. The structure of aniline is a hybrid of five contributing species because of the conjugation of unshared electron pair with the aromatic ring, whereas we can write only two Kekule structures for anilinium cation. Since resonance stabilizes an aromatic amine more than it stabilizes its ammonium cation, the proton acceptability and thereby basic strength of aromatic amines would be less. It may also be argued that due to resonance, unshared electrons on nitrogen in aromatic amines are less available for sharing with a proton– a feature opposite to that in alkyl amines.

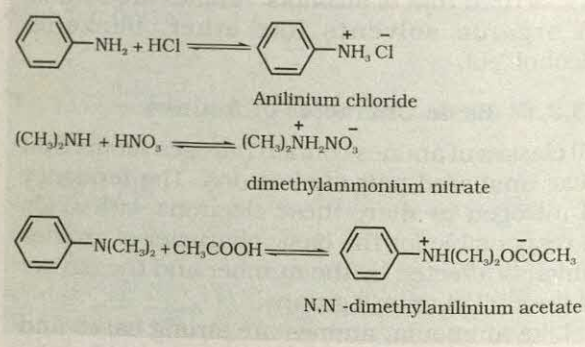


An electron releasing group present in an aromatic amine ring especially in *o*/*p* position, stabilises the ammonium cation formed after protonation of amine and hence increases the basic strength of aromatic amine. An electron-withdrawing group adversely affects the stability of an aromatic ammonium cation and decreases the basic strength of parent aromatic amine. The electron releasing and withdrawing groups will also, respectively, enhance and decrease the availability of unshared electrons on nitrogen and thereby basic strength of aromatic amines.

15.2.7 Chemical Reactions of Amines

The reactions of amines are mainly due to participation of unshared pair of electrons of nitrogen which makes them react as a nucleophile or a base. A nucleophile is a species that attacks an electron-deficient carbon and a base is a species that attacks an electron-deficient hydrogen i.e., proton. In aromatic amines, the same unshared pair of electrons facilitates electrophilic substitution in the phenyl ring. The number of hydrogen atoms on the amine nitrogen also affects the course of some reactions. Some reactions of amines are described below:

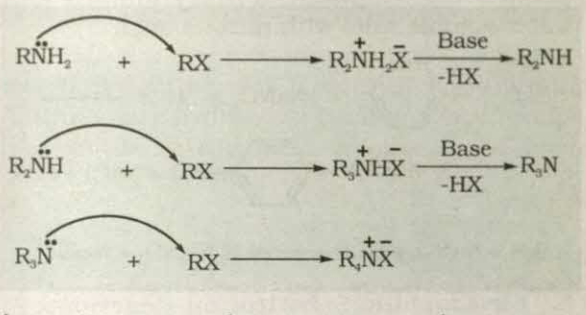
1. Salt Formation: Amines, being basic react with acids to form salts.



These salts are usually soluble in water which on treatment with aqueous hydroxide regenerate the amines.

2. Alkylation: A primary or secondary amine, as a nucleophile performs nucleophilic substitution at an alkyl halide. On removal of HX, a secondary or a tertiary amine is generated respectively and the former being a more powerful nucleophile again reacts similarly with

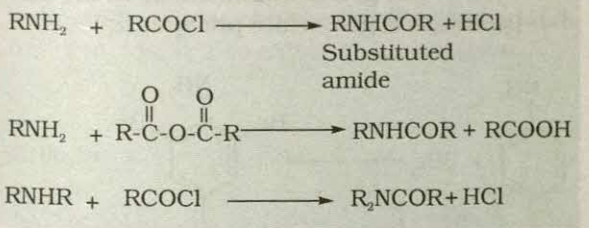
the organic halide to form tertiary amine. At each stage of these reactions, an equivalent amount of a strong acid is generated. It can protonate the amine making unshared pair of electrons unavailable for nucleophilic attack and stop the reaction before completion. Thus, for neutralization of the acid and for liberating the nucleophile, a base such as a carbonate is added. Finally, the tertiary amine reacts with alkyl halides to form a quaternary ammonium salt.



Aromatic amines also react in a similar manner.

3. Acylation: Aliphatic and aromatic primary and secondary amines undergo acylation through nucleophilic substitution of acid derivatives such as acid halides or anhydrides to form amides.

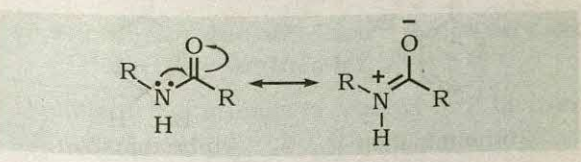
During the reaction, the acid generated can



form salt of the amine which thus will lose nucleophilic character and the reaction will not proceed to completion. So a base is added to facilitate the reaction.

Unlike in the case of alkylation reaction of amines, the amide formed here does not react further with organic halide because the amide is non-basic and a poor nucleophile due to its nitrogen unshared pair of electrons being in conjugation with carbonyl group.

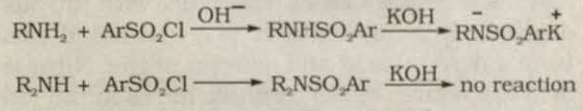
Amongst the acid derivatives, acid chlorides



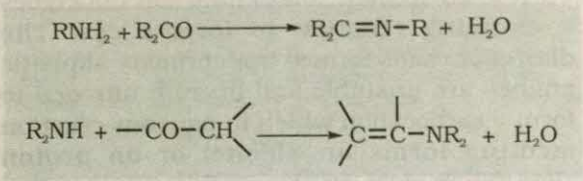
are stronger acylating agents than the anhydrides and esters react very slowly. Carboxylic acids as such form only salts with amines and not the amides.

Tertiary amines fail to react with acid derivatives because they cannot lose a proton to stabilize the product. So in acylation reaction of an amine, in addition to its nucleophilic character, presence of an H atom on nitrogen is also necessary.

Aliphatic and aromatic primary and secondary amines react with acid chlorides of sulphonic acids to form secondary and tertiary sulphonamides. The former having *pKa* about 10, is as acidic as phenol and is freely soluble in aqueous KOH. It can be recovered from the solution by acidification. The tertiary sulphonamide lacking H on nitrogen is insoluble in aqueous KOH. Tertiary amines do not react with benzenesulphonyl chloride. Benzene sulphonyl chloride is known as **Hinsberg's reagent** and is used for separation of primary, secondary and tertiary amines.

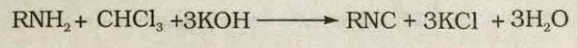


4. Reactions with Carbonyl Compounds: Primary amines react with aldehydes and ketones to yield imines also called Schiff bases. Aldehydes and ketones that have alpha protons react with secondary amines to form enamines.

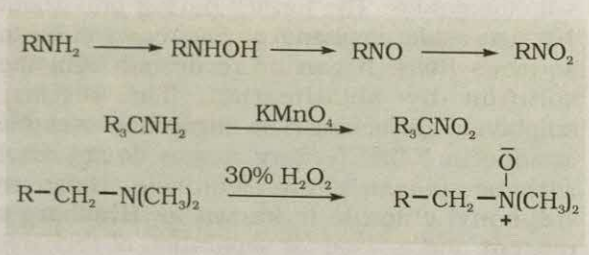


The double bond in both imines and enamines, can be reduced by catalytic hydrogenation or sodium cyanoborohydride reduction to form corresponding amines. (Section 15.2.4)

5. Carbylamine Reaction: When a primary amine is warmed with chloroform and alcoholic potash, an alkyl isocyanide (carbylamine) is formed which gives an offensive smell. Since this reaction is not given by secondary and tertiary amines, it is used for distinguishing primary amines from other classes of amines.

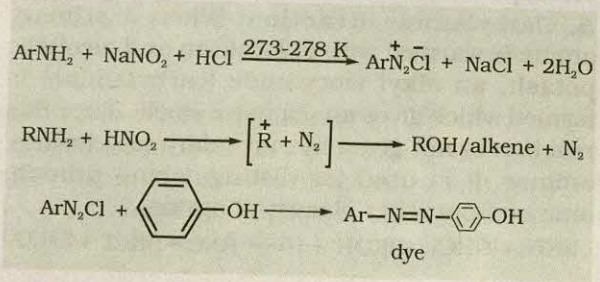


6. Oxidation of Amines: Primary amines undergo oxidation to nitro compounds through a sequence of steps given below. Depending on the reagent, various species such as hydroxylamine, nitroso or nitro compounds are formed. Primary amine having $-NH_2$ group at a tertiary carbon is oxidized with potassium permanganate to a nitro compound in excellent yield. Such a nitro compound is not easily prepared in any other way. Treatment of a tertiary amine with hydrogen peroxide affords an amine oxide.



7. Reactions with Nitrous Acid: The three classes of amines react differently with nitrous acid which being unstable is generated in situ from a mineral acid and sodium nitrite. Nitrous acid is a source of electrophilic nitrosonium ion $O{=}N^+$ which reacts with amines.

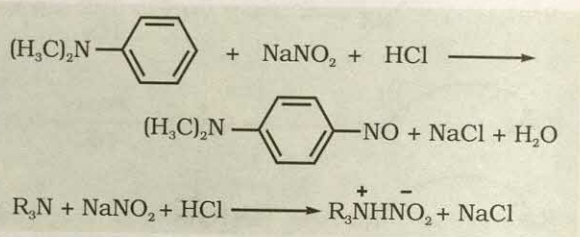
Primary aromatic amine reacts with nitrous acid to form a diazonium salt which is stable in low temperature reaction conditions and is an important species for many laboratory and industrial operations. On reaction with phenol, an aromatic diazonium salt undergoes a coupling reaction to form a dye. The diazonium salts formed from primary aliphatic amines are unstable and liberate nitrogen to form a carbocation which in aqueous reaction medium forms an alcohol or on proton elimination gives an alkene. Since on reaction with nitrous acid only aliphatic primary amines liberate nitrogen, this reaction can be used for distinguishing them from other amines.



Secondary amines, both aliphatic and aromatic, on reaction with nitrous acid give yellow coloured oily *N*- nitrosoamines which unlike amines are insoluble in aqueous mineral acids. This character can be used as a test for secondary amines.

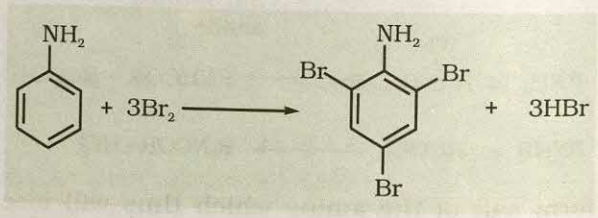
$$R_2NH + NaNO_2 + HCl \longrightarrow R_2N - N = O + NaCl_2 + H_2O$$

Aromatic tertiary amines on reaction with nitrous acid, undergo electrophilic substitution with nitrosonium ion at the *p*-position of the phenyl ring. Aliphatic tertiary amines form water-soluble salts with nitrous acid.

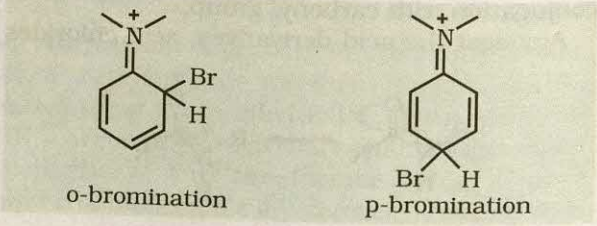


8. Electrophilic Substitution Reactions: All amino groups, $-NH_2$, -NHR, $-NR_2$ are most powerful activating groups in aromatic electrophilic substitution reactions and are ortho and para directing.

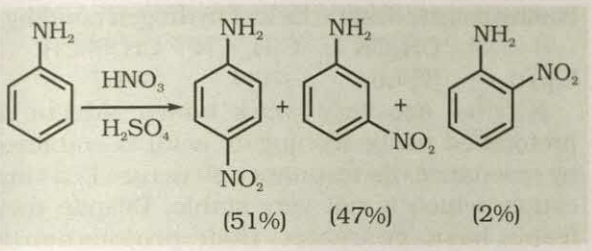
Aniline like phenol, under very mild conditions, even in the absence of a catalyst, instantaneously gets brominated, at all the three *o, p*-positions to give white precipitate.



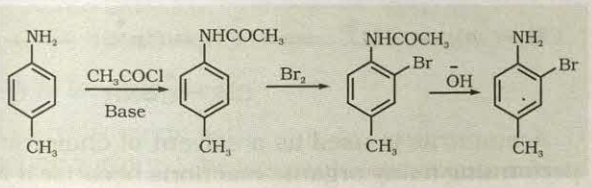
This high reactivity is due to the fact that, in addition to other resonating structures that stabilize intermediate carbocation in aromatic electrophilic substitution, following structures formed due to interaction of nitrogen unshared pair of electrons with the positively charged ring also contribute to the stability of the intermediates in *o,p*-bromination.



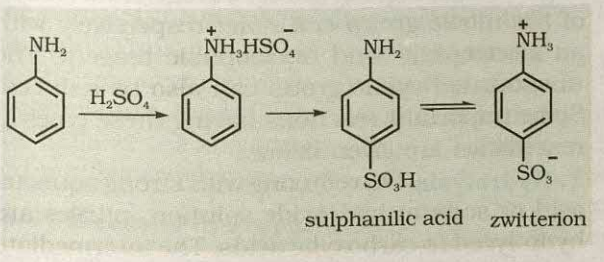
Nitration of aniline, unexpectedly gives 47% m-nitroaniline. It is due to the fact that – NH_2 group in aniline gets protonated to *m*-directing and deactivating $^+NH_3$ group.



For facilitating nitration, aromatic amines are converted to amides which after performing nitration are hydrolysed back to amino groups. For controlling the bromination also, the amide derivatives are used.



Aniline is sulphonated by heating, anilinium hydrogen sulphate formed from aniline and sulphuric acid at 453-473 K and the product, p-amino benzenesulphonic acid commonly called sulphanilic acid is obtained as the product. Like amino acids, it also exists as a zwitterion.



15.2.8 Distinction between Primary, Secondary and Tertiary Amines

The three classes of amines (1°, 2° and 3°) can be distinguished by carbylamine test, nitrous acid test and Hinsberg's reagent test as discussed earlier.

15.2.9 Separation of Primary, Secondary and Tertiary Amines (cf 15.2.7.3)

The mixture of amines is reacted with benzene sulphonyl chloride and the product mixture obtained is treated with aq. HCl and filtered. The filtrate which contains tertiary amine as its hydrochloride is isolated as amine by additon of base. The acid insoluble residue is treated with aq. KOH solution and filtered. The filtrate on acidification gives the sulphonamide of primary amine which is isolated after hydrolysis. The sulphonamide insoluble in alkali, is hydrolysed to get secondary amine.

15.3 CYANIDES AND ISOCYANIDES

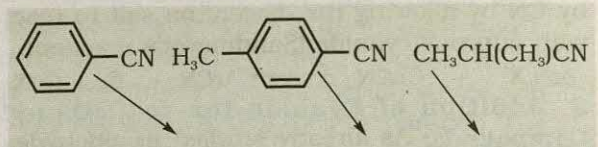
15.3.1 Cyanides

Cyanides are a class of compounds which have -CN as the functional group and can be regarded as derived from HCN by replacement of H by R/Ar. Unlike HCN and KCN, organic cyanides are much less toxic.

15.3.2 Nomenclature

In the common mode of nomenclature not used that frequently, the suffix cyanide is added to the alkyl or aryl group. Generally, they are named by replacing the *-ic* or *-oic* (in case of benzoic acid) or *-onic* (in case of propionic acid), from the name of the carboxylic acid with the same number of carbon atoms including the nitrile carbon, by *-onitrile*. In IUPAC system, suffix nitrile is added to the name of the hydrocarbon. For determining the position of the substituent in a chain, the nitrile carbon is numbered as 1. Some examples of nomenclature using these systems are given below.

	CH_3CN	CH_3CH_2CN	$CH_2{=}CHCN$
Common Names	methyl cyanide	ethyl cyanide	vinyl cyanide
	acetonitrile	propionitrile	acrylonitrile
IUPAC Names	ethanenitrile	propanenitrile	prop-2-ene-nitrile

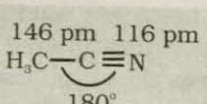


Common Names	phenyl cyanide	tolyl cyanide	isopropyl cyanide
	benzonitrile	*p*-toluonitrile	isobutyronitrile
IUPAC Names	benzene carbonitrile	4-methyl benzene carbonitrile	2-methyl propanenitrile

15.3.3 Structure

Organic cyanides possess one sigma and two pi bonds between C and N atoms and constitute a triple bond as found in alkynes. Thus, nitrogen here is *sp* hybridized. The C-C≡N bond angle is 180°. Bond length of the triple bond in C≡N is

shorter than the double bond C=N in imines and C-N single bond in amines. The structure of acetonitrile is shown below:



15.3.4 Methods of Preparation of Nitriles

The usual way of preparing nitriles is by nucleophilic displacement of the halogen in alkyl/aryl halides and the diazo group in aryl diazonium salts with cyanide from inorganic cyanide. HCN is a source of –CN group when added to carbonyl compounds. Primary amides on dehydration are also converted to nitriles.

1. Nucleophilic Substitution of Alkyl Halides: Aliphatic nitriles are prepared by treatment of alkyl halides with potassium cyanide in a solvent that will dissolve both the reactants. Since cyanide ion is a strong base, in case of tertiary halides elimination is the principal reaction and with secondary halides both substitution and elimination products are formed.

$$RX + KCN \longrightarrow RCN + KX$$

$$CH_3CH_2Br + CN^- \longrightarrow CH_3CH_2CN \text{ (substitution)} + Br^-$$

$$(CH_3)_3CBr + CN^- \longrightarrow (CH_3)_2C{=}CH_2 \text{ (elimination)} + Br^- + HCN$$

2. Substitution of Diazonium Salts: Aromatic nitriles are not formed from unreactive aryl halides but are prepared from aryl diazonium salts through replacement of diazonium group by CN by allowing the diazonium salt to react with cuprous cyanide (Sandmeyer's reaction).

$$ArN_2X + CuCN \longrightarrow ArCN + N_2 + CuX$$

3. Addition of Cyanide Ion to Carbonyl Compounds: As already studied in aldehydes and ketones (Unit 14), they form cyanohydrins with HCN.

4. Dehydration of Primary Amides: When a primary amide is treated with a strong dehydrating agent such as phosphorous pentoxide, it is converted to the corresponding nitrile. A variety of other dehydrating agents such as thionyl chloride, phosphorous pentachloride, acetic anhydride etc. can also be used.

$$RCONH_2 + P_4O_{10} \xrightarrow{-H_2O} RCN + \text{Complex phosphates}$$

15.3.5 Physical Properties

Nitriles are amongst the most polar organic compounds. Acetonitrile has dipole moment 3.4D. Due to high polarity, nitriles have rather higher boiling points, despite lack of hydrogen bonding.

	CH_3CN	C_2H_5CN	$CH_3C{\equiv}CH$
b.p/K	354.6	370.4	244.7

Nitriles are very weak bases. Although protonated nitrile (conjugate acid) is stabilized by resonance, its resonance structure is a vinyl cation, which is not very stable. Despite their feeble basic character, their protonation is important in their acid catalysed reactions. Due to this weak basic nature, nitriles are very poor hydrogen bond acceptors. Nevertheless, acetonitrile is miscible with water and propionitrile has low solubility in water. Higher nitriles are insoluble in water.

$$CH_3{-}C{\equiv}N + H_3O^+ \rightleftharpoons CH_3{-}C{\equiv}\overset{+}{N}H \longleftrightarrow CH_3{-}\overset{+}{C}{=}NH + H_2O$$

Acetonitrile is used as a solvent of choice for performing many organic reactions because it is not reactive in mild acidic and basic conditions. Having high polarity it is capable of dissolving a variety of reactants. It has moderate boiling point and can be easily removed. It is miscible with water and a number of organic solvents.

15.3.6 Chemical Reactions

In general, of organic nitrile, nitrogen and carbon of the nitrile group can react respectively with an electrophilic and nucleophilic reagent. The unsaturated cyano group can also be reduced. Some important reactions having these types of reactivities are given below.

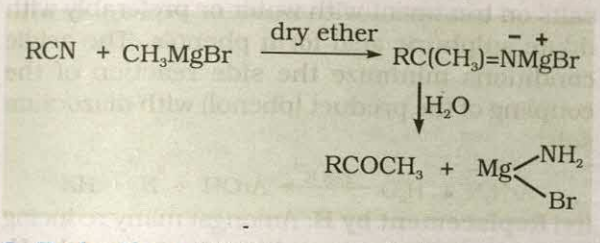
1. Hydrolysis: On refluxing with strong aqueous acid or sodium hydroxide solution, nitriles are hydrolyzed to carboxylic acids. The intermediate in both the reactions is the primary amide. By using alcohol under acidic conditions, an ester is obtained.

$$C_6H_5CN + HCl \xrightarrow{\text{reflux}} C_6H_5COOH$$

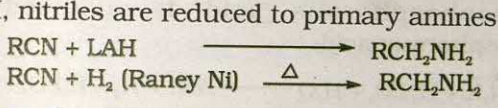
$$C_6H_5CN + NaOH_{(aq.)} \xrightarrow[H^+]{\text{reflux}} C_6H_5COOH$$

$$C_6H_5CN + HCl\ (g) \text{ in } CH_3OH \xrightarrow{\text{reflux}} C_6H_5{-}C(OCH_3){=}\overset{+}{N}H_2Cl^- \xrightarrow{H_2O} C_6H_5COOCH_3$$

2. Reaction with Grignard Reagent: On addition of nucleophilic Grignard reagent, the initially formed imine derivative is hydrolyzed to form a ketone. This reaction offers a neat route to obtain ketones as esters always react further with Grignard reagent to form tertiary alcohols.



3. Reduction: Nitriles need relatively stronger reagents for reduction. Catalytic hydrogenation in presence of Raney nickel or on reduction with LAH, nitriles are reduced to primary amines.



15.3.7 Isocyanides

They are isomeric with cyanides and have -NC functional group. The isocyanide group also has a triple bond but constitutes a dipolar species in which nitrogen has a positive charge and carbon has a negative charge ($R\text{-}N^{+}\equiv C^{-}$). This is opposite to the characters of carbon and nitrogen in cyanide group.

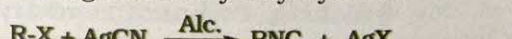
15.3.8 Nomenclature

For naming isocyanides, the word *iso* is prefixed to the name of the corresponding cyano/nitrile compound. Thus, CH_3NC is named as methyl isocyanide or acetoisonitrile. In another mode of nomenclature, the suffix carbylamine is added to the name of the alkyl group. Thus, CH_3NC is called methylcarbylamine.

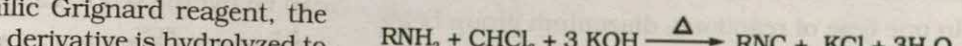
15.3.9 Methods of Preparation

Isocyanides are generally prepared from alkyl halides or primary amines.

1. From Alkyl Halides: When an alkyl halide is heated with silver cyanide, Ag^{+} facilitates the removal of halide ion. A mixture of alkyl isocyanide and alkyl cyanide is formed in which the former is the predominant species. It may be recalled that alcoholic KCN gives mainly alkyl cyanide.

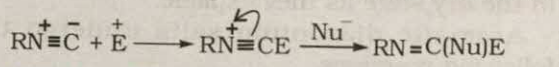


2. From Primary Amines: Both aromatic and aliphatic primary amines, on heating with chloroform and aqueous potassium hydroxide form isonitriles.

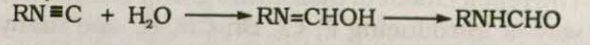


15.3.10 Chemical Reactions

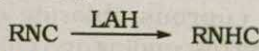
In an isocyanide, first an electrophile and then a nucleophile add at the carbon to form a species which usually undergoes further transformations:



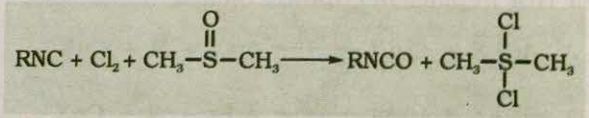
1. Addition of Water: Acid catalysed addition of water gives alkyl formamide derivative.



2. Reduction with LAH: With LAH as well as on catalytic hydrogenation, isocyanides are reduced to *N*-methylamines.



3. Oxidation: Isocyanides are oxidised to isocyanates, on reactions with HgO or with ozone as well as with a halogen and DMSO (dimethyl sulphoxide).

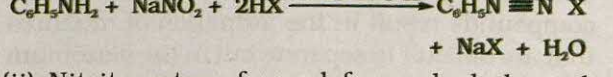


15.4 DIAZONIUM SALTS

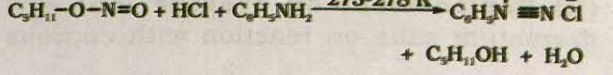
Diazonium salts have structure $ArN_2^{+}X^{-}$. Functional group is attached to an aryl group and are intermediates in the preparation of many types of compounds. They find major use in dye industry.

15.4.1 Methods of Preparation

(i) When aromatic primary amines taken in ice cold aqueous mineral acid are treated with sodium nitrite (a source of nitrous acid), diazonium salts are formed. Due to their instability, the salts are not generally stored and are used immediately after their preparation. The conversion of a primary amine into a diazonium salt is called diazotisation.



(ii) Nitrite esters formed from alcohols and nitrous acid, are also used to generate diazonium salts on treatment with aromatic primary amines.



15.4.2 Chemical Reactions

In one type of reactions, diazonium group being a very good leaving group is substituted by other groups. In the second type, being positively charged, it behaves as an electrophile and couples with electron-rich aromatic systems to give the azo compounds. They are rarely isolated in the dry state as they explode.

Aromatic diazonium salts undergo the following reactions.

1. Replacement Reactions

The replacement of diazonium group is a general way of introducing F, Cl, Br, CN, H, and many other groups in the aromatic ring.

(i) Replacement by halide ion: The solution of freshly prepared aromatic diazonium salt on reaction with cuprous chloride or cuprous bromide gives corresponding aryl chloride or aryl bromide. This reaction is called **Sandmeyer reaction**. Alternatively, the same reaction can be performed by using copper powder and HCl or HBr in place of cuprous halide.

$$ArN_2^+X^- + CuCl \xrightarrow{HCl} ArCl + N_2 + CuX$$

$$ArN_2^+X^- + CuBr \xrightarrow{HBr} ArBr + N_2 + CuX$$

Aromatic diazonium salts and potassium iodide react to give aryl iodides. Here, the use of cuprous halide is not required.

$$ArN_2^+X^- + KI \longrightarrow ArI + N_2 + KX$$

Replacement by fluoride ion is carried out in a different manner. On addition of fluoroboric acid to a solution of diazonium salt, the diazonium fluoroborate precipitates out. It is quite stable and is isolated. When heated to dryness , it loses boron trifluoride and nitrogen gas and aryl fluoride is formed.

$$ArN_2^+X^- + HBF_4 \rightarrow ArN_2^+BF^- \xrightarrow{heat} ArF + BF_3 + N_2$$

For preparing aryl halides, this method is very advantageous. Aryl chlorides and bromides when obtained by direct halogenation of aromatic compounds result in the formation of mixtures that are difficult to separate but in the diazonium salt replacement method, a pure single product is formed. It also provides synthetic route for the preparation of aryl iodides and fluorides which are not obtained by direct halogenation.

(ii) Replacement by cyanide ion: Aryl diazonium salts on reaction with cuprous cyanide form corresponding aryl nitriles which can be hydrolysed to carboxylic acids.

$$ArN_2^+X^- + CuCN \xrightarrow{KCN} N_2 + CuX + ArCN \xrightarrow{Hydrolysis} ArCOOH$$

This method of preparing carboxylic acids is more useful than carbonation of Grignard reagents.

(iii) Replacement by OH: Aromatic diazonium salts on treatment with water or preferably with dilute sulphuric acid form phenols. The acidic conditions minimize the side reaction of the coupling of the product (phenol) with diazonium salt.

$$ArN_2^+X^- + H_2O \xrightarrow{298\ K} ArOH + N_2 + HX$$

(iv) Replacement by H: Amongst many reducing agents that can replace diazonium group by H, hypophosphorous acid is used advantageously. In this reaction, nitrogen is evolved and hypophosphorous acid is oxidised to phosphorous acid.

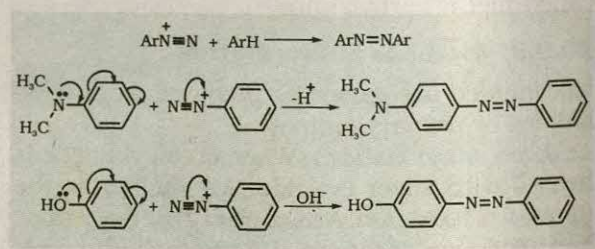
$$ArN_2^+X^- + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HX$$

The reaction can even be performed with amines by using sodium nitrite and hypophosphorous acid as diazotising reagent. This reaction is used for removing NH_2 group from an aromatic ring.

2. Coupling of Diazonium Salts

Formation of Azo Compounds: The diazonium ion is an electrophile as there is positive charge on terminal nitrogen. It can react with nucleophilic aromatic compounds (Ar–H) activated by electron-donating groups (-OH and -NH_2), which as strong nucleophiles react with aromatic diazonium salts to give coloured azo compounds. The nitrogen of the diazonium group is retained in the product. This reaction is called **coupling** and is an **electrophilic substitution reaction** as given below.

$$ArN_2^+ + ArH \longrightarrow ArN{=}NAr$$

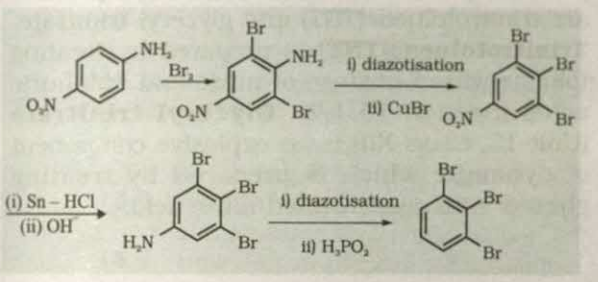


15.4.3 Importance of Diazonium Salts in Synthetic Organic Chemistry

As depicted in their chemical reactions, aryl diazonium salts constitute intermediates that can be used to synthesize many classes of organic

compounds, especially the aryl halides in pure state as given below.

1,2,3-Tribromo benzene which is not formed in pure state by direct bromination of benzene, is obtained by the following sequence of reactions starting from p-nitroaniline. Here, use is made of the orientation effect of $-NO_2$ and $-NH_2$ groups. These groups are removed afterwards to obtain final product.



15.5 SOME COMMERCIALLY IMPORTANT COMPOUNDS

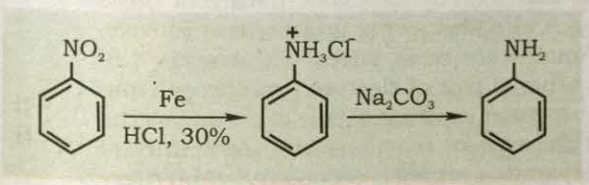
Amines

The chief commercial use of amines is as intermediates in the synthesis of dyes and synthetic fibres. These are also used as medicines due to their physiological and psychological effects.

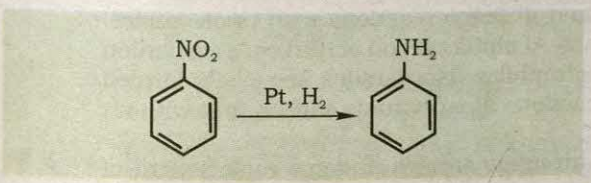
1. Aniline: It is one of the most important of all the amines. It is manufactured by the reduction of nitrobenzene using;

(a) iron-filings and hydrochloric acid, and

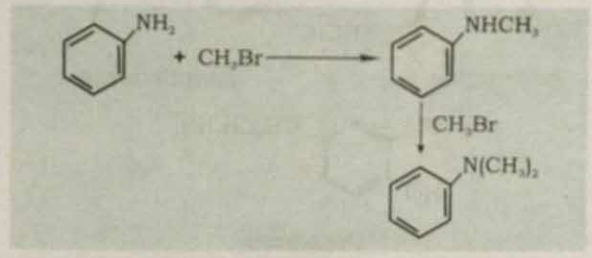
(b) catalytic hydrogenation.



Catalytic hydrogenation of nitro group takes place smoothly with hydrogen gas in presence of finely divided nickel or platinum as catalyst.

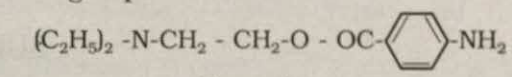


2. *N*, *N*-Dimethylaniline (DMA): It is used as a raw material in the preparation of a number of azo dyes, for example, methyl orange, crystal violet-malachite green, etc. It couples readily to give p-azo derivatives. DMA is prepared by methylation of aniline with bromomethane (Section 15.2.7)



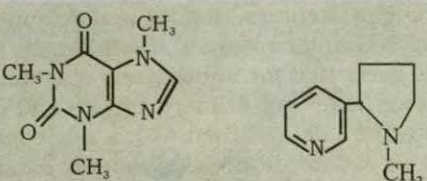
3. 1,6-Hexamethylenediamine: It is used as a raw material in the production of nylone-66 (Unit 16, Class XII).

4. Novocaine: It is also called procaine and is used as a local anaesthetic. It was developed in 1905 and contains a primary and a tertiary amino groups.



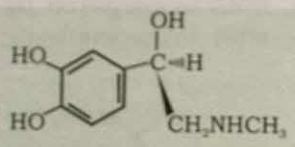
Novocaine

A number of N containing compounds which act as bases occur in nature. These are known as alkaloids. In these compounds, nitrogen may be present in the form of primary, secondary and tertiary amino group. Most of the alkaloids produce striking physiological effect. Caffeine–a central nervous system stimulant, occurs in tea leaves, coffee bean and cola nut, nicotine (present in tobacco plant), atropine (present in Atropa belladonna) and cocaine (present in Erythroxylum coca) are some examples of alkaloids. In small doses, **nicotine acts as a stimulant, but in larger doses, it causes depression, nausea and vomitting**. Atropine is an intense poison. In 0.5 - 1.0% concentration, it is used to dilate the pupil of the eye in ophthalmic examinations. In small doses, cocaine decreases fatigue and increases mental activity. Prolonged use of cocaine leads to physical addiction and to periods of deep depression.

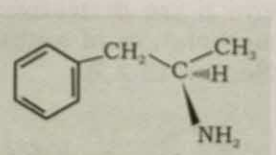


Caffeine Nicotine

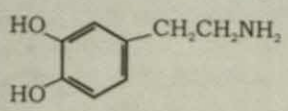
A large number of medically and biologically important compounds are amines. A few examples are given as follows:



Adrenaline



Amphetamine



Dopamine

Adrenaline, a hormone, is released into the blood stream when an animal senses danger. It causes an increase in blood pressure and a widening of passages of the lungs. All these effects prepare the animal to fight or to flee. **Amphetamine** is a powerful stimulant. **Dopamine** is a neurotransmitter in the brain. Abnormalities in the level of dopamine cause many psychological disorders. Dopamine also plays an important role in regulation and control of movement, motivation and cognition.

Two important nitrogen containing explosives are trinitrotoluene(TNT) and glyceryl trinitrate. **Trinitrotoluene(TNT)** is prepared by treating toluene with a mixture of nitric and sulphuric acids (Section 15.1.2). **Glyceryl trinitrate** (Unit 13, Class XII) is an explosive component of dynamite which is prepared by treating glycerol with concentrated nitric acid.

SUMMARY

The nitro compounds are easily obtained in the pure state. The nitro group influences the reactivity of attached alkyl or aryl group and the functional groups present on them. Thus, acidic strength of phenols and reactivity of aryl halides towards nucleophilic substitution are enhanced if a nitro group is present on their o/p positions. In aliphatic nitro compounds, a carbanion can be generated easily and reactions performed to obtain various products including ketones.

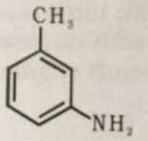
Amines, usually formed from nitro compounds, halides, ketones, amides, imides etc., exhibit hydrogen bonding which influences their physical properties. In alkyl amines, a combination of electron releasing, steric and H-bonding factors influence the stability of their ammonium cations in protic polar media and thereby the basic nature of these amines. In aromatic amines, electron releasing and withdrawing groups, respectively, increase and decrease their basic character. Amines are weak bases. The reactions of amines are governed by the availability of the unshared pair of electrons on nitrogen and proceed by initial attack of electrophiles and subsequent transformation to products. The influence of the number of hydrogen at N, on the type of reactions and the nature of products is responsible for distinguishing and separating primary, secondary and tertiary amines. The amino and acetylamino groups enhance the reactivity of the aromatic ring towards electrophiles.

Organic cyanides are not unsafe to use and acetonitrile, the first member of the series, is a solvent of choice for performing organic reactions. They are usually obtained from halides, ketones, amides and diazonium salts and undergo reactions with nucleophiles. With Grignard reagent, they uniquely form ketones. At alpha carbon of nitriles, a carbanion is generated for subsequent reactions with electrophiles. Isocyanides are easily formed from halides or primary amines and undergo reactions at isocyanide carbon first with an electrophile and then with a nucleophile.

Aryl diazonium salts, usually obtained from aromatic amines undergo replacement of the diazonium group with a variety of nucleophiles to provide advantageous methods for forming aryl halides, cyanides, phenols and reductive removal of amino group and thus constitute useful synthetic reagents. Coupling reactions of aryl diazonium salts with phenols or amines form an important class of dyes.

EXERCISES

15.1 Give the common and IUPAC names of the following compounds:

(a) 

(b) $O_2NCH_2CH_2OH$

(c) $CH_3CH(NO_2)CH_2CH_3$

15.2 Write structures for the following compounds:

(a) TNT
(b) Picric acid
(c) *p*-nitrotoluene
(d) Azoxybenzene
(e) Benzene diazonium chloride
(f) Sulphanilic acid

15.3 Why do nitro compounds have higher boiling points than the hydrocarbons having almost same molecular mass?

15.4 How do you prepare p-nitroaniline from aniline?

15.5 Explain what happens when aniline reacts with a mixture of sulphuric acid and nitric acid?

15.6 How is nitrobenzene converted to aniline under neutral conditions?

15.7 Explain why does nitrobenzene on nitration with nitric acid and sulphuric acid form only m-dinitrobenzene?

15.8 How will you prepare 1-nitropropene-1 from acetaldehyde?

15.9 How can you convert 2-nitropropane to acetone?

15.10 Explain why is nucleophilic substitution of p-nitrochlorobenzene easier than that of chlorobenzene?

15.11 Write structures for the following compounds:

(a) Butyronitrile (b) Phenylacetonitrile (c) Propylcarbylamine.

15.12 Why is acetonitrile preferred as a solvent for running organic reactions?

15.13 Explain the role of mineral acid in the reaction of a carbonyl compound with aq. KCN.

15.14 How is it that a ketone reacts with Grignard reagent to form a tertiary alcohol but in the reaction of a nitrile with Grignard reagent, a ketone is formed?

15.15 How will you convert acetonitrile to propionitrile?

15.16 How does an isocyanide react with an electrophile and a nucleophile at the same isocyanide carbon? Give an example.

15.17 How will you convert benzonitrile to acetophenone ($C_6H_5COCH_3$)?

15.18 Draw structures for the following compounds.

(a) N-isopropylaniline (b) *p*-toluidine (c) *t*-butylamine.

15.19 Arrange following sets in order of their basic strength:

(a) Ethylamine, Ammonia and Triethylamine
(b) Aniline, *p*-nitroaniline, *p*-toluidine.

15.20 How will you prepare a pure sample of a primary amine from a primary alkyl halide?

15.21 How will you convert an alkyl halide into a primary amine having one more carbon than the alkyl halide used?

15.22 How can a carboxylic acid be converted to an amine having one carbon atom less than the carboxylic acid used?

15.23 Explain the observed K_b order : $Et_2NH > Et_3N > EtNH_2$, in aqueous solution.

15.24 What will be the basic strength order of $EtNH_2$, Et_2NH, Et_3N in gas phase ? Explain.

15.25 Why are amines less acidic than comparable alcohols?

15.26 Why are primary amines higher boiling than tertiary amines?

15.27 Why are aromatic amines weaker bases than aliphatic amines?

15.28 How can you find out whether a given amine is a primary amine? Write the chemical reaction involved in the test you perform.

15.29 How can you separate a mixture of primary, secondary and tertiary amines? Write chemical reactions involved in the process.

15.30 How do aromatic and aliphatic tertiary amines react with nitrous acid?

15.31 How do aliphatic primary and secondary amines react with nitrous acid?

15.32 Explain how does the presence or absence of hydrogen on N of amines affect the modes of their reactions with nitrous acid?

15.33 How will you prepare ethyl amine from acetaldehyde?

15.34 Amino group is o,p-directing for aromatic electrophilic substitution. Why does aniline on nitration gives a substantial amount of m-nitroaniline?

15.35 Why does bromination of aniline, even under very mild conditions give 2,4,6-tribromoaniline instantaneously?

15.36 How can you convert p-toluidine to 2-bromo-4-methylaniline ?

15.37 How can you convert aniline to iodobenzene?

15.38 How can you get benzonitrile from aniline?

15.39 Why is an amide more acidic than an amine?

UNIT 16

POLYMERS

OBJECTIVES

After studying this Unit, you will be able to:

- appreciate that some simple small molecules called monomers undergo repeated addition/ condensation reactions to form high molecular mass species called macromolecules or polymers.
- learn about the formation of polymers by different modes.
- appreciate that a large variety of articles of daily use are made from polymers.

"Copolymerization has been used by nature in polypeptides which may contain as many as 20 different amino acids. Chemists are still far behind, but copolymers or terpolymers are now being widely produced."

Polymers are macro-sized molecules of relatively high molecular mass, which find extensive use in our daily life. They are obtained by joining together a large number of small molecules. Structurally, they are characterised by many repeating molecular units which form linear chains or a cross-linked network. Starting from n molecules of a compound M, linking in a linear manner will form polymer x-M-$(M)_{n-2}$-M-y. The nature of linkages at the terminal units i.e., M-x and M-y depends upon the mode of reaction used in making the polymer.

The process of formation of polymers from their starting materials is called **polymerization** and the small molecules that combine with each other are termed as **monomers**. A polymer may be made by polymerization of a large number of one or more compounds. Thus, polythene is made only from ethylene (ethene) but nylon-66 is made from H_2N-$(CH_2)_6$-NH_2 (hexamethylene diamine) and HOOC $(CH_2)_4$ COOH (adipic acid).

$\left(CH_2\text{-}CH_2\right)_n$ $\left(NH\text{-}(CH_2)_6\text{-}NHCO\text{-}(CH_2)_4\text{-}CO\right)_n$

polythene nylon-66

16.1 CLASSIFICATION OF POLYMERS

16.1.1 Classification Based on Source of Availability

1. Naturally Occurring Polymers

These occur in plants and animals and are very essential for life. For example, proteins constitute much of the animal body, nucleic acids control heredity at molecular level, cellulose provides food, clothing and shelter (Unit 17) and rubber provides various articles of daily use.

2. Semi synthetic Polymers

These are mostly derived from naturally occurring polymers by chemical modifications. Cellulose on acetylation with acetic anhydride in the presence of sulphuric acid forms cellulose diacetate used in making threads and materials like films, glasses etc. Vulcanized rubber has much improved properties and is used in making tyres etc. Gun-cotton, which is cellulose nitrate, is used in making explosives.

3. Synthetic Polymers

A large number of man-made polymers are now available. These include fibres, plastics and synthetic rubbers etc., and find diverse uses as in clothing, electric fittings, eye lenses, substitute for wood and metals.

16.1.2 Classification Based on Mode of Polymerization

1. Homopolymers and Copolymers

Polymers when made by polymerization of a single monomeric chemical species are known as **homopolymers**. When the polymers are synthesised by polymerization of two or more than two different monomers, they are called **copolymers**. Polythene formed from ethylene is a homopolymer. When styrene and butadiene are polymerised together, it gives the copolymer called styrene-butadiene rubber.

$$n\,H_2C{=}CH_2 \longrightarrow \underset{\text{polythene}}{\left(-CH_2-CH_2-\right)_n} \quad \text{(Homopolymer)}$$

$$\underset{\text{butadiene}}{n\,CH_2{=}CH{-}CH{=}CH_2} + \underset{\text{styrene}}{x\,C_6H_5{-}CH{=}CH_2} \longrightarrow$$

$$\underset{\text{styrene-butadiene rubber}}{-\left(CH_2{-}CH{=}CH{-}CH_2\right)_n-\left(CH_2{-}\underset{C_6H_5}{CH}\right)_x} \quad \text{(Copolymer)}$$

2. Addition and Condensation polymers

Synthetic polymers are also classified according to their mode of formation and are distinguished as addition polymers and condensation polymers. Addition polymers are formed by reactions between monomer molecules possessing double or triple bonds. Polythene formed by addition of ethylene molecules to each other and styrene-butadiene rubber formed by addition reactions between butadiene and styrene are addition polymers. The condensation polymers are formed by condensations between monomeric units with the elimination of small molecules such as water, ammonia, alcohol etc.

Nylon-66 is formed by condensation between hexamethylene diamine and adipic acid (16.2.2).

$$n\,H_2N(CH_2)_6NH_2 + n\,HOCC(CH_2)_4COOH \longrightarrow \underset{\text{Nylon-66}}{-(NH(CH_2)_6NHCO(CH_2)_4CO)-} + n\,H_2O$$

Example 16.1
Is $+CH_2\text{-}CH\,(C_6H_5)+_n$, a homopolymer or a copolymer? Is it an addition or a condensation polymer?

Solution
It is a homopolymer and the monomer from which it is obtained is styrene, $C_6H_5{-}CH{=}CH_2$. Since the monomer contains a double bond, it forms an addition polymer.

16.1.3 Classification Based on Molecular Forces

Polymers have been classified into the following four categories on the basis of the magnitude of intermolecular forces present in them.

1. Elastomers

In elastomers, the polymer chains are held together by the weakest intermolecular forces. These weak forces permit the polymer to be stretched. A few– 'cross links' are introduced in between the chains, which help the polymer to retract to its original position after the force is released, as in vulcanized rubber.

2. Fibres

The polymers which are used for making fibre, possess high tensile strength and high modulus. This can be attributed to the strong intermolecular forces like hydrogen bonding which, for example, operate in polyamides (nylon-66). These strong forces also lead to close packing of chains and thus, impart crystalline nature. As a result, these polymers show sharp melting points.

3. Thermoplastics

The intermolecular forces of attraction in thermoplastic polymers are intermediate between elastomers and fibres. As a result, these can be easily moulded by heating. In thermoplastic polymers, there is no cross-linking between chains. Some common thermoplastics are polyethylene, polystyrene, etc.

4. Thermosetting Polymers

These polymers are normally made from relatively low molecular mass semi-fluid polymers which on heating in a mould become

infusible and form an insoluble hard mass. This happens due to extensive cross-linking between different polymer chains forming three-dimensional network of bonds (bakelite).

16.2 GENERAL METHODS OF POLYMERIZATION

Two major methods generally used for preparing polymers are – **addition** and **condensation** polymerization.

16.2.1 Addition Polymerization

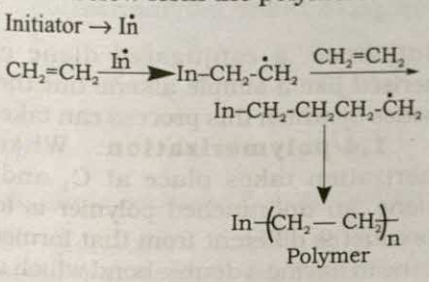
When the molecules of same monomer or different monomers simply add together to form a polymer, this process is called addition polymerization. The monomers used here are unsaturated compounds such as alkenes, alkadienes and their derivatives. This mode of polymerization can take place through formation of either radicals or ionic species such as carbanions and carbocations. This process is also called **chain growth polymerization** because it takes place through stages leading to increase of chain length and each stage produces reactive intermediate for use in the next stage of the growth of the chain. Such free radical and ionic addition polymerizations are discussed below.

16.2.2 Free Radical Addition Polymerizations

A variety of unsaturated compounds, alkenes or dienes and their derivatives are polymerized by this process. Polymerization of ethylene takes place through radicals, which are generated by an initiator. These initiators are molecules, which decompose to provide radicals easily. t- Butyl peroxide is a commonly used initiator because it decomposes under mild conditions to form t-butoxide radical.

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{373\text{-}423\ K} 2(CH_3)_3CO^{\bullet}$$

Here the reactive intermediate is a free radical that adds to a monomer molecule to form a new free radical of larger size. Such repeated addition as depicted below form the polymers..

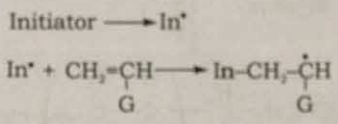


a. Vinyl Polymerization

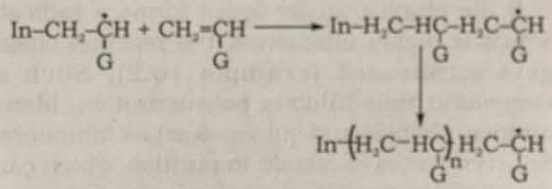
Most of the commercial addition polymers are vinyl polymers obtained from alkenes and their derivatives $CH_2{=}\underset{G}{CH}$.

This type of polymerization is performed by heating the monomer with only a very small amount of the initiator or by exposing the monomer to light. The process of polymerization starts with the addition of the radical formed from the initiator to the alkene double bond generating a new radical and this step is called chain initiating step. As this radical reacts with alkene, another bigger sized radical is generated. The repetition of this sequence with new and bigger radicals propagates the reaction and this step is termed as chain propagating step. Ultimately, at some stage the product radical thus formed reacts with another radical to form the polymeric product. This step is called chain-terminating step. This general mode of radical polymerization of vinyl monomers is depicted below:

Chain initiation steps

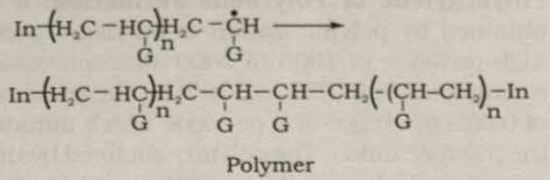


Chain propagating step



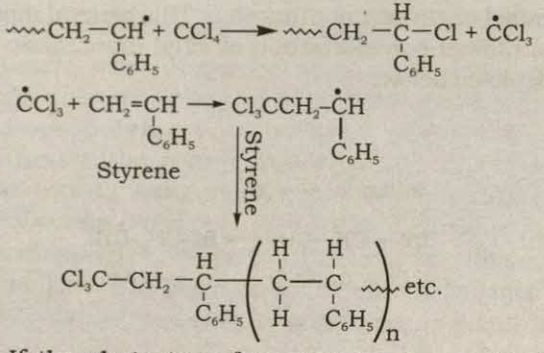
For termination of chain, these free radicals can combine in different ways to form the polymer. One mode of termination of chain is shown as under:

Chain terminating step



In vinylic polymerizations, various other reactions of free radicals with some other compounds present may compete with the

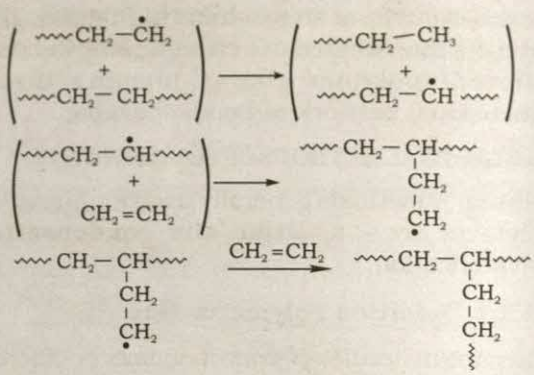
parent addition chain reactions. One such reaction takes place with molecules that can react with the growing chain to interrupt the further growth of the original chain. But again the product of such a reaction may initiate its own chain growth. This leads to the lowering of the average molecular mass of the polymer. Such reagents are called **chain transfer agents** and include carbon tetrachloride, carbon tetrabromide, etc. For example, in the presence of carbon tetrachloride, styrene polymerizes to form polystyrene of a lower average molecular mass which also contains some chlorine. What happens here is that growing polystyrene radical which normally would add on a monomer reacts with the chain transfer agent to end the original chain and produces a new radical. The latter initiates a new polymerization chain and thereby forms a new polymer as depicted below.



If the chain transfer agent forms a radical, which is highly unreactive, the reaction chain gets terminated (example 16.2). Such a compound thus inhibits polymerization. Many amines, phenols and quinones act as inhibitors. So, even traces of certain impurities, which can act as chain transfer agent or an inhibitor can interfere with the original polymerization chain reaction. Hence, the monomers should be free from such inhibitors.

Vinylic polymerization is exemplified below by the formation of polythene.

Polyethylene or Polythene Formation: It is obtained by polymerization of ethylene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 to 570 K in the presence of traces of oxygen or a peroxide which initiates the polymerization. The polymer obtained by this procedure of free radical addition and H-atom abstraction has highly branched structure and is called **low density polythene**. Its mode of formation is depicted below:



Low density polythene is chemically inert, tough but flexible and poor conductor of electricity. Hence, it is used in insulation of electric wires, manufacturing of squeeze bottles, toys and flexible pipes.

When polymerization of ethylene is carried out in the presence of a catalyst at about 330 to 350 K at atmospheric pressure, the polymer obtained has a linear structure and is called **high density polythene**. It is also chemically inert but relatively tough and hard with high tensile strength and is used in the manufacture of containers, house wares, bottles, pipes, etc.

Some examples of commonly used polymers formed by this method in the category of homopolymers and their applications in daily life are given in the table of section 16.5.

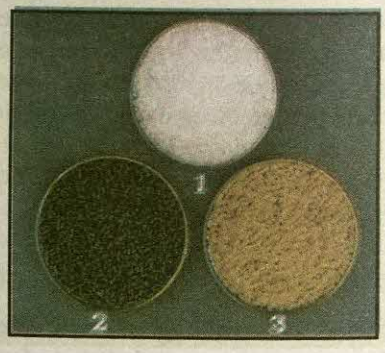


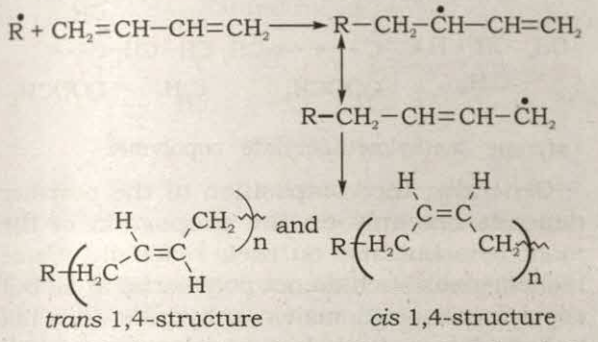
Fig. 16.1 *High density polythene granules. (1) is natural form; (2) and (3) are coloured with dyes.*

b. Conjugated Diene polymerization

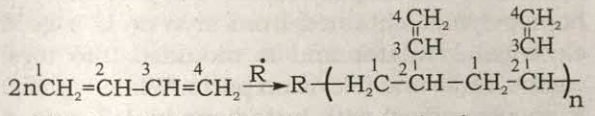
1,3-Butadiene, a conjugated diene can be polymerised like a simple alkene but there are two modes by which this process can take place.

1. 1,4-polymerization: When the polymerization takes place at C_1 and C_4 of butadiene, an unbranched polymer is formed. This product is different from that formed from an alkene in having a double bond which at each

of its carbons is substituted by different groups and hence can exist either as trans-polybutadiene or cis-polybutadiene or a mixture as shown below:



2. 1,2-polymerization: Alternatively, 1,3-butadiene can undergo polymerization at C_1 and C_2 to yield the polymeric product, polyvinyl polythene.

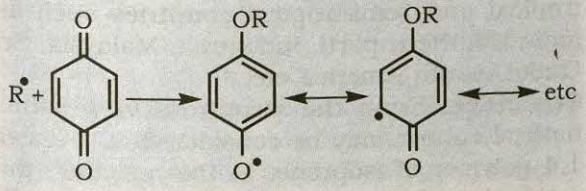


The double bonds in these initial polymers can be linked by further treatment with chemicals to modify the properties of the polymers. These reactions form the basis of the formation of rubbers.

Solution

Example 16.2
How does the presence of benzoquinone inhibit the free radical polymerization of a vinyl derivative?

Benzoquinone traps the radical intermediate to form a non-reactive radical, which is highly stabilized by resonance. Because of the lack of reactivity of this intermediate, further progress of the chain reaction is interrupted and the reaction stops.



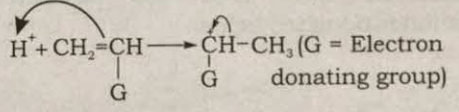
16.2.3 Ionic Addition Polymerization

Vinylic monomers can undergo addition polymerization through the formation of ionic intermediates instead of the free radicals. Here, the initiator instead of a free radical source would be an ion source. The general modes of both these ionic polymerizations are discussed below.

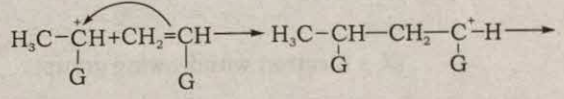
a. Cationic Addition Polymerization

When the initiator is cationic in nature, on addition to the double bond, it would generate a cationic intermediate for propagating the addition chain process and is termed as cationic polymerization. The process is initiated by an acid. In the chain initiation step, the acid adds on the double bond to form a cation. On further addition to the double bond, a bigger cation is formed and sequence of steps propagates the chain to the polymeric cation. The chain termination can take place by loss of the proton. These stages of polymerization are depicted below:

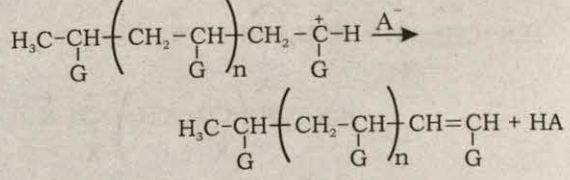
Chain initiation step



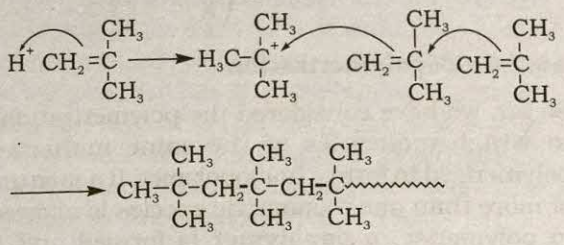
Chain propagating step



Chain terminating step



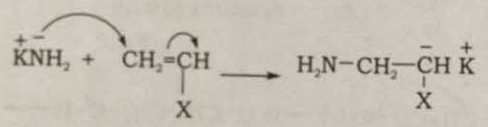
Cationic polymerization is facilitated in monomers containing electron-releasing groups. Thus, isobutylene undergoes cationic polymerization easily as it has two electron releasing $-CH_3$ groups that will stabilize the intermediate cation.



b. Anionic Addition Polmerization

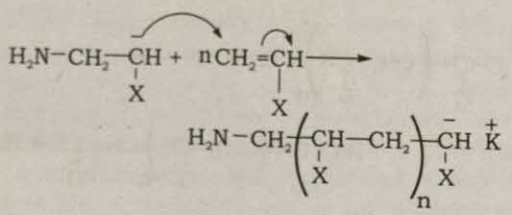
An anionic initiator will similarly generate carbanionic intermediate and the resulting polymerisation is categorized as anionic addition polymerization. Here, the active centre of the propagating species is negatively charged. Hence, it occurs easily with monomers containing electron-withdrawing groups such as phenyl, nitrile etc., which are able to stabilize the propagating species. Initiation can be brought about by reagents such as n-butyl lithium or potassium amide. In the initiation step, the base adds to the double bond to form a carbanion. In the chain propagation, this carbanion adds to the double bond and the process goes on getting repeated to form a polymeric carbanion. The chain reaction can be terminated by the addition of an acid. The formation of polystyrene from styrene in the presence of potassium amide is an important example of this category of polymerization. The mode of anionic polymerization is depicted below.

Chain initiation step

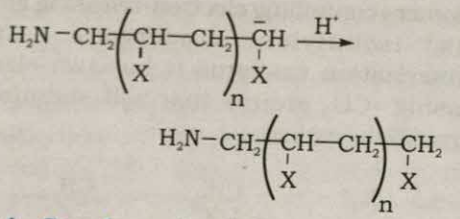


(X = Electron withdrawing group)

Chain propagating step

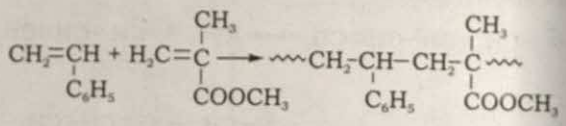


Chain terminating step



16.2.4 Copolymerization

So far, we have considered the polymerizations in which molecules of the same monomer polymerised to form a homopolymer. If a mixture of more than one monomeric species is allowed to polymerise, a **copolymer** is formed and it contains multiple units of each monomer used in the same polymeric chain. For example, a mixture of styrene and methyl methacrylate can form a copolymer.



styrene methylmethacrylate copolymer

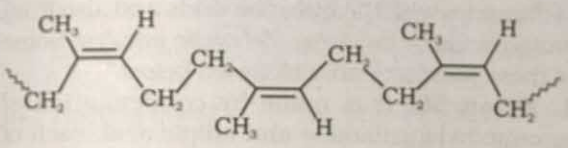
Generally, the composition of the polymer depends not only on the proportion of the monomers but also on their reactivity. Some monomers as such do not polymerize at all but copolymerize, e.g., maleic anhydride does not polymerize as such but copolymerizes with styrene in a highly symmetrical manner to form styrene maleic anhydride copolymer.

Copolymers have properties quite different from the homopolymers. Polystyrene, a homopolymer obtained from styrene is a good electrical insulator and is moulded into toys, combs, radio and television parts. When styrene, is copolymerized with butadiene in 1:3 ratio, a copolymer of styrene-butadiene rubber (SBR) is obtained (Section 16.5). It is very tough and is a good substitute for natural rubber. It possesses high abrasion resistance, high load-bearing capacity and is used for the manufacture of auto tyres. Its other uses include floor tiles, footwear components, cable insulations etc.

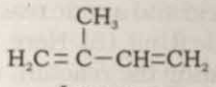
16.2.5 Natural Rubber

It is a natural polymer and possesses remarkable elasticity. It undergoes long range reversible extension under relatively small applied force. This elasticity makes it valuable for a variety of uses. It is manufactured from rubber latex which is a colloidal suspension of rubber in water and is obtained by making incisions in the bark of rubber trees found in tropical and semi-tropical countries such as India (southern part), Indonesia, Malaysia, Sri Lanka, South America etc.

Structure: From the structural view-point, natural rubber may be considered as a linear 1,4 polymer of isoprene. In this polymer, the residual double bonds are located between C_2 and C_3 of isoprene units in the polymer. All these double bonds have *cis* configurations and thus, rubber is *cis* 1,4-polyisoprene.



Natural rubber

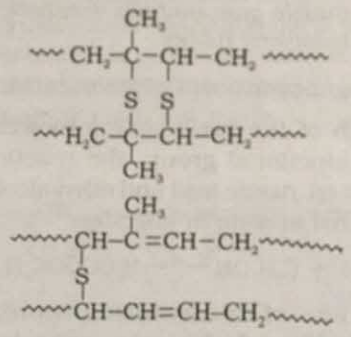


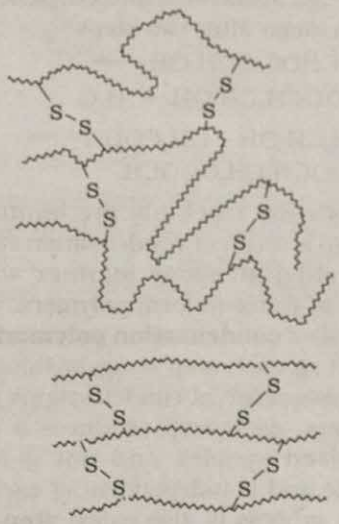
Isoprene

In the structure of rubber, there are no polar substituents. Hence, intermolecular attractions are largely limited to van der Waals interactions. These interactions are again weak because all cis configurations about double bonds do not let the polymer chains come close enough for effective attraction. Thus, the *cis*- polyisoprene molecule is not a straight chain but has a coiled structure. Consequently, it can be stretched like a spring. On stretching, the molecules become partially aligned with respect to each other and on releasing the force, the chain reverts back to its original coiled state.

16.2.6 Vulcanization of Rubber

Rubber as such is used in the temperature range 283 to 335 K as it becomes soft at higher temperatures and brittle at low temperatures. It has large water absorption capacity, is non-resistant to nonpolar solvents and is attacked by oxidizing agents. Accidentally, in 1893, Charles Goodyear discovered that addition of sulphur to hot rubber causes changes that improve its physical properties in a spectacular manner. This process is called **vulcanization**. It was originally performed by heating a mixture of raw rubber and sulphur at 373 to 415 K. This process is slow and additives such as zinc oxide etc., are used to accelerate the rate of vulcanization. The vulcanised rubber has excellent elasticity, low water-absorption tendency, resistance to oxidation and organic solvents. The double bonds in the rubber molecules, in addition to determining their configurations act as reactive sites. The allylic $-CH_2-$, alpha to double bond is also very reactive. On vulcanization, sulphur establishes cross-links at these reactive sites. Thus, the rubber gets stiffened and intermolecular movement of rubber springs is prevented resulting in change of physical character of rubber. The extent of stiffness of vulcanized material depends upon the amount of sulphur added. Thus, about 5% sulphur is used for making tyre rubber and 30% of it for making battery case rubber. The detailed mode of vucanization process may be difficult to visualize, but probable structures of vulcanized rubber molecules are depicted below.





16.2.7 Synthetic Rubbers

Majority of these polymers are derived from butadiene derivatives and contain carbon-carbon double bonds so that they can also be vulcanized by the processes developed for natural rubber. Thus, synthetic rubbers are either homopolymers of 1,3-butadiene derivatives or are copolymers in the formation of which one of the monomers is 1,3- butadiene or its derivative so that the polymer has the availability of double bonds for its vulcanization. Structures and applications of commonly used synthetic rubbers, namely, Buna-S, Buna-N, neoprene and Butyl rubber are given in Section 16.5.

Fig. 16.2 *Bubble gum contains synthetic styrene-butadiene rubber.*

16.2.8 Condensation Polymerization

When each of the two reacting molecules has only one functional group, the reaction stops after one step. Acetic acid and ethyl alcohol react to form ethyl acetate in one step:

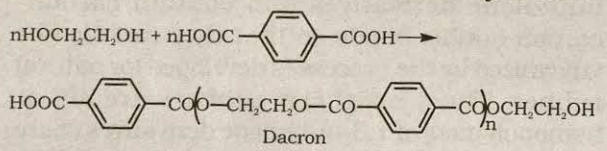
$$H_3CCOOH + C_2H_5OH \longrightarrow H_3CCOOC_2H_5 + H_2O$$

When one of the reacting molecules is bifunctional and the other one is monofunctional, e.g., acetic acid and ethylene-glycol, the reaction stops after two steps:

$$H_3CCOOH + HOCH_2CH_2OH \longrightarrow H_3CCOOCH_2CH_2OH + H_2O \quad (i)$$

$$H_3CCOOCH_2CH_2OH + CH_3COOH \longrightarrow H_3CCOOCH_2CH_2OCOCH_3 \quad (ii)$$

When both the reactants are bifunctional, they undergo a series of condensation reactions in a controlled stepwise manner with the elimination of water to form polymers, and the process is called **condensation polymerization**. The product of each step is again bifunctional so that the sequence of condensations goes on and on. Thus, each step produces a distinct functionalised species and not a reactive intermediate and is independent of each other. Hence, this process is also called **step-growth polymerization** as is evident in the following example of polymerization of ethylene glycol-a diol with terephthalic acid– a dicarboxylic acid.



Dacron

Some important condensation polymerizations, distinguished by their linking units are described below:

a. Polyamides

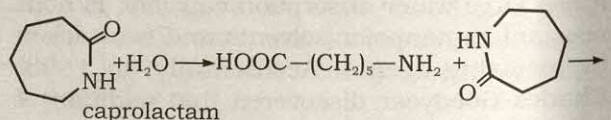
Polymers possessing amide linkages are important synthetic fibres. They are made by condensation of diamines with dicarboxylic acids and also from amino acids or lactams, the cyclic amides. Some of these polymers are discussed below.

1. Nylon 66: It is made by condensation of hexamethylenediamine and adipic acid, each of which possesses six carbon atoms and these numbers are represented in the name of the product as 66. Acid and amine react to form a salt and not the amide (Unit 15). Here, the polyamide is formed by heating the reactant mixture under pressure and the process has been developed so that the molecular mass of the polymer is controlled in the range 12000 to 20000.

$$HOOC(CH_2)_4COOH + NH_2(CH_2)_6NH_2 \longrightarrow \text{Salt} \xrightarrow[-H_2O]{\text{Heat}} \longrightarrow \left(NH(CH_2)_6NHCO(CH_2)_4CO\right)_n$$

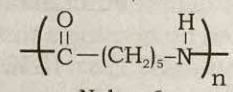
Nylon 66

2. Nylon 6: It is formed by self-condensation of a large number of molecules of amino caproic acid. The amino acid has six carbon atoms and this number is again represented in the name of the product. Since caprolactam is more easily available, it is used for polymerization which is carried out in the presence of water that first hydrolyses the lactam to amino acid. Subsequently, the amino group of the amino acid can react with the lactam and the process goes on and on to form the polyamide polymer as depicted below:



caprolactam

$$HOOC-(CH_2)_5-HN-CO-(CH_2)_5-NH_2$$

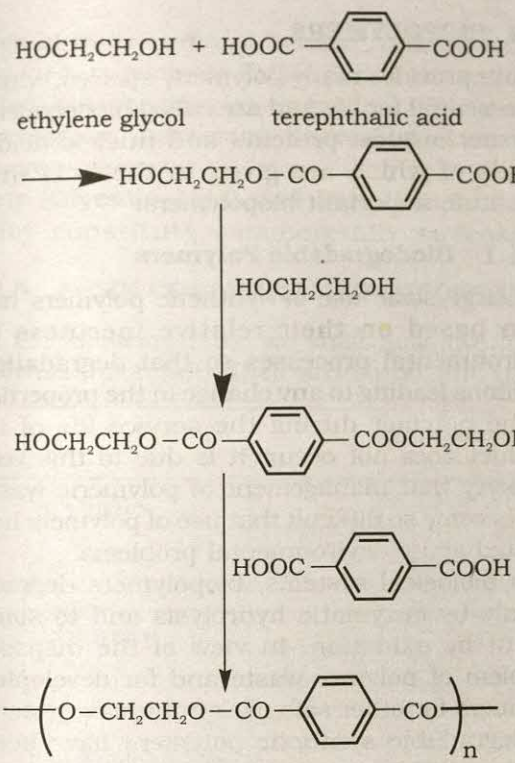


Nylon 6

Nylons are insoluble in common solvents, have good strength and absorb little moisture. These are primarily used for making fibres used in manufacture of garments, carpets, ropes and tyres etc.

b. Polyesters

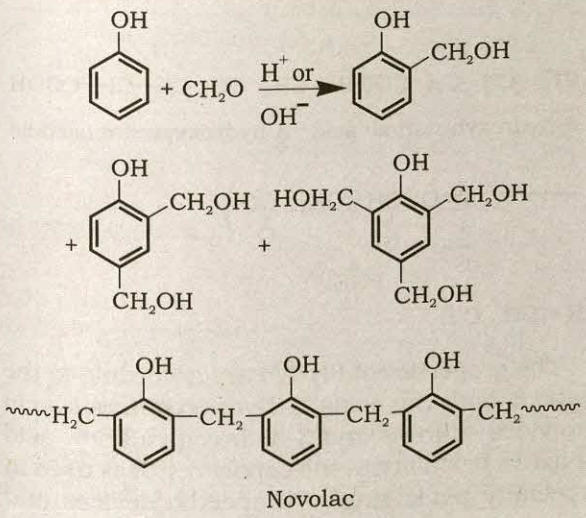
Dacron is the best known of the polyesters and is manufactured from ethylene glycol and terephthalic acid. The reaction is carried out at 420 to 460 K in the presence of a catalyst-mixture of zinc acetate and antimony trioxide.



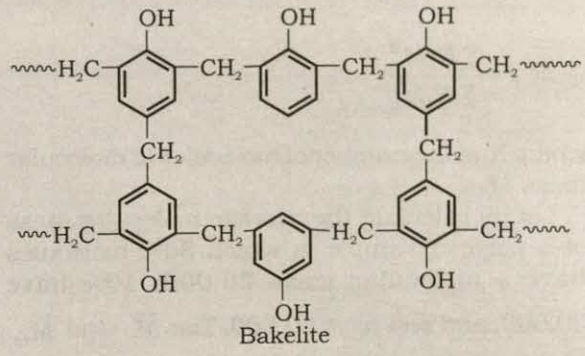
The Terylene fibre (Dacron) is crease - resistant and has low moisture absorption. It has high tensile strength. It is mainly used in making wash and wear garments, in blending with wool to provide better crease and wrinkle resistance.

c. Phenol-formaldehyde polymer (Bakelite and related polymers)

These are the oldest synthetic polymers and are still extensively used. Phenol is condensed with formaldehyde in the presence of either an acid or a base. The reaction starts with the initial formation of *o* and/or *p*-hydroxymethyl phenol derivatives, which further react with phenol to form compounds where rings are joined to each other with $-CH_2$ groups. The initial product could be a linear product – Novolac.

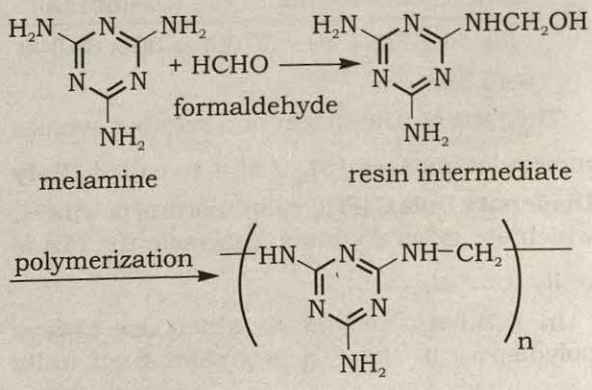


On further heating with formaldehyde, novolac undergoes cross-linking to an infusible solid. This polymer called bakelite is hard, scratch and water resistant. It possesses excellent electrical insulating character and hence, it finds major use in making electrical goods.



d. Melamine-formaldehyde resins

Melamine and formaldehyde copolymerise to give polymer used in making plastic crockery. Cups and plates made from melamine polymer are hard and do not break on dropping.



16.3 MOLECULAR MASS OF POLYMERS

Generally, a polymer sample contains chains of varying lengths and, therefore, its molecular mass is always expressed as an average. In contrast, natural polymers such as proteins contain chains of identical length and hence, have definite molecular mass.

Number average and weight average molecular masses

The molecular mass of a polymer is expressed as number average molecular mass ($\overline{M}_n$) or weight average molecular mass ($\overline{M}_w$).

Here $\overline{M}_n$ and $\overline{M}_w$ are defined by the following equations:

$$\overline{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

where N_i is the number of molecules of molecular mass M_i.

Let us calculate the average molecular mass of a polymer sample in which 30% molecules have a molecular mass 20,000; 40% have 30,000; and rest have 60,000. The $\overline{M}_n$ and $\overline{M}_w$ of this sample will be:

$$\overline{M}_n = \frac{(30\times 20{,}000)+(40\times 30{,}000)+(30\times 60{,}000)}{(30+40+30)}$$

$$= 36{,}000$$

$$\overline{M}_w = \frac{30(20{,}000)^2 + 40(30{,}000)^2 + 30(60{,}000)^2}{30\times 20{,}000 + 40\times 30{,}000 + 30\times 60{,}000}$$

$$= 43{,}333$$

The ratio of the weight and number average molecular masses ($\overline{M}_w / \overline{M}_n$) is called **'Poly Dispersity Index'** (PDI). Some natural polymers, which are generally monodispersed, the PDI is unity (i.e., $\overline{M}_w = \overline{M}_n$).

In synthetic polymers, which are always polydispersed, the PDI is greater than unity because $\overline{M}_w$ is always higher than $\overline{M}_n$. $\overline{M}_n$ is determined by employing methods which depend upon the number of molecules present in the polymer sample, viz., colligative property like osmotic pressure. On the other hand, methods such as light scattering and ultra-centrifuge depend on the mass of the individual molecules and yield weight-average molecular masses.

16.4 BIOPOLYMERS

Nature provides many polymeric species, which are essential for life and are called biopolymers. Polysaccharides, proteins and nucleic acids, details of which are given in the next unit constitute important biopolymers.

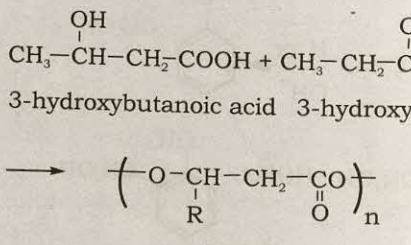
16.4.1 Biodegradable Polymers

The large scale use of synthetic polymers has been based on their relative inertness to environmental processes so that degradation reactions leading to any change in the properties of the polymer during the service life of its product does not occur. It is due to this very property that management of polymeric waste has become so difficult that use of polymers has created acute environmental problems.

In biological systems, biopolymers degrade mainly by enzymatic hydrolysis and to some extent by oxidation. In view of the disposal problem of polymer waste and for developing polymers for other safe uses in human system, biodegradable synthetic polymers have been developed. These synthetic polymers mostly have functional groups prevalent in biopolymers and lipids.

Aliphatic polyesters are one important class of biodegradable polymers as several of them are commercially potential biomaterials. Some examples are described below.

Poly β–Hydroxybutyrate-co-β-Hydroxyvalerate (PHBV): It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid, in which the monomer units are connected by ester linkages.



3-hydroxybutanoic acid 3-hydroxypentanoic acid

PHBV

R = CH_3, C_2H_5

The properties of PHBV vary according to the ratio of both the acids. 3-Hydroxybutanoic acid provides stiffness and 3-hydroxypentanoic acid imparts flexibility to the copolymer. It is used in specialty packaging, orthopaedic devices and

even in controlled drug release. When a drug is put in a capsule of PHBV, it is released only after the polymer is degraded. PHBV also undergoes bacterial degradation in the environment.

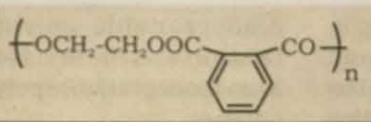
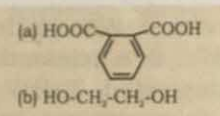
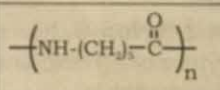
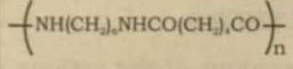
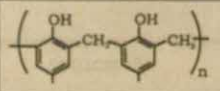
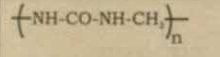
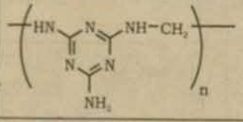
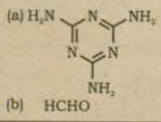
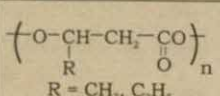
Poly (Glycolic Acid) and Poly (Lactic Acid): They constitute commercially successful biodegradable polymers such as sutures. Dextron was the first bioabsorbable suture made from biodegradable polyesters for post-operative stitches.

Nylon-2-Nylon-6. It is an alternating polyamide copolymer of glycine and amino caproic acid and is biodegradable.

16.5 SOME COMMERCIALLY IMPORTANT POLYMERS

In the following table we shall now give a brief account of the various commercially important polymers alongwith their structures and uses.

S. No.	Name of Polymer	Structure	Monomer	Uses
1.	Polythene	$+CH_2-CH_2+_n$	$CH_2 = CH_2$	As insulator, anticorrosive, packing material, household and laboratory wares.
2.	Polystyrene	$+CH(C_6H_5)-CH_2+_n$	$CH(C_6H_5)=CH_2$	As insulator, wrapping material, manufacture of toys and household articles.
3.	Polyvinylchloride (PVC)	$+CH_2-CHCl+_n$	$CH_2 = CHCl$	In manufacture of raincoats, hand bags, vinyl flooring and leather clothes.
4.	Polytetrafluoro ethylene (PTFE) or Teflon	$+CF_2-CF_2+_n$	$CF_2 = CF_2$	As lubricant, insulator and making cooking wares.
5.	Polymethyl metha acrylate (PMMA) or Plexi glass	$+CH_2-C(CH_3)(COOCH_3)+_n$	$CH_2=C(CH_3)COOCH_3$	As substitute of glass and making decorative materials.
6.	Polyacrylonitrile (Orlon)	$+CH_2-CH(CN)+_n$	$CH_2 = CHCN$	In making synthetic fibres and synthetic wool.
7.	Styrene butadiene rubber (SBR or BuNa-S)	$+CH_2-CH=CH-CH_2-CH(C_6H_5)-CH_2+_n$	(a) $CH_2=CH-CH=CH_2$ (b) $CH(C_6H_5)=CH_2$	In making automobile tyres and footwear.
8.	Nitrile rubber (Buna-N)	$+CH_2-CH=CH-CH_2-CH(CN)-CH_2+_n$	(a) $CH_2=CH-CH=CH_2$ (b) $CH(CN)=CH_2$	In making oil seals, manufacture of hoses and tank linings.
9.	Neoprene	$+CH_2-C(Cl)=CH-CH_2+_n$	$CH_2=C(Cl)-CH=CH_2$	As insulator, making conveyor belts and printing rollers.
10.	Poly ethyl acrylate	$+CH_2-CH(COOC_2H_5)+_n$	$CH_2 = CH-COOC_2H_5$	In making films, house pipes and finishing fabrics
11.	Terylene (Dacron)	$+OC-C_6H_4-COO-CH_2-CH_2O+$	(a) HOOC-C_6H_4-COOH (b) HO-CH_2-CH_2-OH	For making fibres, safety belts, tyre cords, tents etc.

12.	Glyptal		 (a) HOOC, COOH; (b) HO-CH_2-CH_2-OH	As binding material in preparation of mixed plastics and paints.
13.	Nylon 6			In making fibres, plastics, tyre cords and ropes.
14.	Nylon 66		(a) HOOC-$(CH_2)_4$-COOH (b) H_2N-$(CH_2)_6$-NH_2	In making brushes, synthetic fibres, parachutes, ropes and carpets.
15.	Bakelite		(a) HCHO	For making gears, protective coating and electrical fittings.
16.	Urea formaldehyde resin		(a) HCHO (b) NH_2CONH_2	For making unbreakable cups and laminated sheets.
17.	Melamine formaldehyde resin		 (b) HCHO	In making plastic crockery, un breakable cups and plates.
18.	Poly-β-hydroxy butyrate -co-β-hydroxy valerate (PHBV)	 R = CH_3, C_2H_5	(a) CH_3-CH(OH)-CH_2-COOH (b) CH_3-CH_2-CH(OH)-CH_2-COOH	As packaging, orthopaedic devices and in controlled drug release.

Giulio Natta
(1903-1979)

Giulio Natta was born in September, 1903 in Imperia, near Genoa, Italy. He obtained a doctorate degree in chemical engineering at Milan Polytechnic in 1924. Together with Karl Ziegler of Germany he was awarded the Nobel Prize of Chemistry in 1963 for the development of *Ziegler - Natta Catalysts*. His work led to the introduction of polypropylene resins through the polymerization of propylene to produce stereoregular polymers. The contribution of Natta to the development of high polymers is of immense use in the manufacture of films, fibres, synthetic rubber, etc. This has provided an important building material towards our current domestic and commercial needs.

SUMMARY

Polymers, the high molecular mass macrosized molecules consisting of repeating units of monomers are of synthetic and natural (Unit 17) origin. Synthetic polymers are classified in respect of their composition, on mode of polymerization and nature of molecular forces.

Addition polymerizations are usually performed on alkenes and their derivatives and proceed through chain growth mechanisms involving radicals, cations and anions as intermediates, for the generation of which initiator light/radicals, acids and bases are respectively used. When a mixture of monomers is polymerized, a copolymer containing multiple units of each monomer is formed. 1,3-dienes can undergo 1,2 or 1,4 polymerization and as compared with the polymers formed from alkenes, the products possess double bonds. Natural rubber is a linear polymer of isoprene, and is vulcanized by heating with

sulphur, which forms bonds at alkene, or allylic reaction sites of different chains establishing cross links. Vulcanized rubber has much improved physical properties. Synthetic rubbers are usually obtained by copolymerization of alkene and 1,3 -butadiene derivatives. Polythene, PVC, orlon, teflon and many synthetic rubbers are formed by polymerization of appropriate alkenes through addition mode.

Condensation polymerization takes place in bi or polyfunctionalised monomers possessing -OH, $-NH_2$, -COOH etc., groups with elimination of H_2O, NH_3 etc., and formation of linkages such as ester, amides, etc. Even electrophilic aromatic substitution of phenols with formaldehyde forms polymers having carbon-carbon linkages. Each condensation step provides a bi or polyfunctionalised product and the polymerization progresses step by step. Nylons, dacron and bakelite constitute some important condensation polymers.

Synthetic polymers due to their inertness to degradation have created environmental problems. Since biopolymers degrade enzymatically, synthetic biodegradable polymers having functional groups such as ester, amide, etc., and also potential for use as sutures, implants, drug release matrices, are developed as alternatives. PHBV, PLLA, Nylon-2-nylon-6 etc., constitute some such materials.

EXERCISES

16.1 Is (-NH-CHR-CO-)n, a homopolymer or a copolymer?

16.2 Could a copolymer be formed in both addition and condensation polymerization or not? Explain with examples.

16.3 Write structure of a reagent used for initiating a free radical chain reaction. How does it act?

16.4 Write the mode of free radical polymerization of an alkene.

16.5 Write structures of monomers used for getting the following polymers.
a. PVC b. Teflon c. PMMA

16.6 Why should one always use purest monomer in free radical polymerization?

16.7 How does the presence of carbon tetrachloride influence the course of vinylic free radical polymerization? Explain with an example.

16.8 Explain how 1,3- butadiene polymerizes by different routes.

16.9 Why does styrene undergo anionic polymerization easily?

16.10 Why is cationic polymerization preferred in case of vinylic monomers containing electron donating groups?

16.11 Will you prefer to polymerize acrylonitrile under anionic or cationic polymerization conditions? Explain your choice.

16.12 Elaborate the structure of natural rubber.

16.13 Depict a free radical mode of addition polymerizaion of isoprene.

16.14 How do double bonds in rubber molecules influence their structure and reactivity?

16.15 How does vulcanization change the character of natural rubber?

16.16 Why are the numbers 66 and 6 put in the name nylon 66 and nylon 6 ?

16.17 Illustrate with equations, how nylon-6 is obtained from caprolactam.

16.18 What is the difference between thermosetting and thermoplastic polymers?

16.19 How is bakelite formed? Explain the reactions with equations.

16.20 Explain the differences between polyacrylates and polyesters.

16.21 What is PHBV?

UNIT 17

BIOMOLECULES

OBJECTIVES

After studying this Unit, you will be able to:

- explain the role of a living cell in the regulation of energy cycle in nature.
- learn about the basic chemistry of important biomolecules e.g. carbohydrates, proteins, nucleic acids and lipids.
- Classify and explain functions of some of the biomolecules present in biological systems e.g. hormones and vitamins.
- describe the secondary and tertiary structures of proteins and the double helical structure of DNA.
- explain genetic code and basic genetic mechanisms, DNA replication, transcription and protein synthesis.

"All biological processes are chemical transformations."

Biomolecules, common to living systems are carbohydrates, proteins, enzymes, lipids, vitamins, hormones, nucleic acids and compounds for storage and exchange of energy such as adenosine triphosphate (ATP). Many of these biomolecules are polymers like the synthetic polymers you have studied in Unit 16. For example, starch, proteins, nucleic acids are condensation polymers of simple sugars, amino acids and nucleotides respectively. Most of the biochemical reactions take place in dilute solutions (pH~7) at body temperature (nearly 37°C) and at 1 atmospheric pressure. Biochemical reactions proceed with striking selectivity and at incredible speed. Most of the biomolecules are very large and extremely complex. Their reactions involve complex mechanisms. Biomolecules are related to the living organisms in the following sequence:

Living organisms → Organs → Tissues → Cells → Organelles → biomolecules (carbohydrates, proteins, lipids, nucleic acids)

Before discussing the chemistry of biomolecules, we would like to know about the sources of energy in plants and animals which are responsible for their growth and maintenance.

17.1 THE CELL AND ENERGY CYCLE

The cell is a fundamental structural and functional unit of living organisms. Just as we need energy to run, jump and think, the cell needs a ready supply of cellular energy for many functions that support these activities. Cells need energy for active transport, to move molecules between the environment and the cell, across cells or within cells. Thus, we need a

supply of energy-rich food molecules that can be oxidized to provide the needed cellular energy. Cells obtain energy by oxidation of molecules like glucose. This oxidation takes place in a complex and controlled way by means of enzymes which are biocatalysts. (Part of the energy in cells is coupled to the formation of ATP (adenosine triphosphate, which serves to drive many chemical reactions inside the cell.)

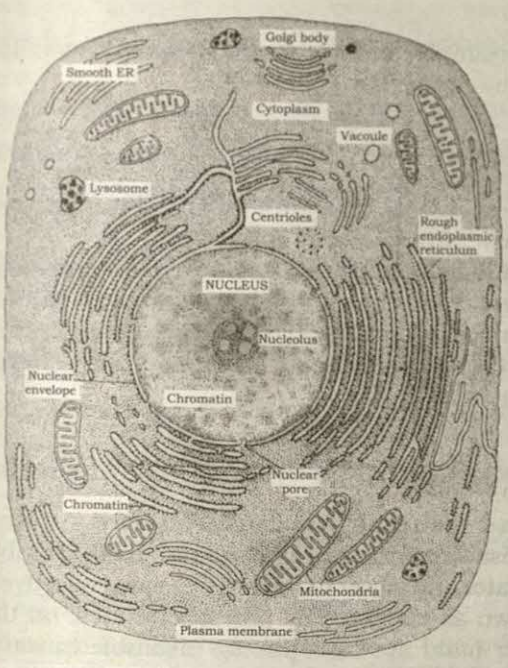


Fig. 17.1 *Structure of Cell.*

There are certain reactions which are endergonic i.e., their Gibbs energy, $\Delta G>0$ and as such appear to be thermodynamically forbidden. Nevertheless, such reactions can be made to proceed in the desired direction by coupling them with some suitable *exergonic reactions* with $\Delta G<0$. Here coupling the reaction means the two reactions are allowed to take place simultaneously. You have already studied in Unit 4 (Section 4.6.4) that conversion of ATP to ADP (Fig. 17.2) (adenosine diphosphate) is highly exergonic ($\Delta G^\circ = -31.0$ kJ mol^{-1}) and can drive any thermodynamically forbidden reaction in the desired direction. This normally happens in several metabolic processes in our body.

17.1.1 Photosynthesis and Energy

Energy for life processes basically comes from Sun. During photosynthesis, green plants absorb energy from the sun to make glucose and oxygen from carbon dioxide, CO_2 and water, H_2O. Photosynthesis is a complex process which occurs in a sequence of steps leading to the net reaction.

$$6CO_2 + 6H_2O + 2880\text{kJ} \xrightarrow{\text{Sunlight}} C_6H_{12}O_6 + 6O_2$$

The oxygen produced in photosynthesis is the source of all the oxygen in our atmosphere. Photosynthesis takes place generally in two series of reactions. Reactions of one series occur only in presence of light energy and are called light reactions. Another series is of *dark reactions* which can occur in dark also, because they do not depend on light energy. The dark reactions proceed on high energy produced by the hydrolysis of ATP. *Chloroplasts* present in the plant cell absorb the released energy. Here, through a series of reactions, water is oxidized to oxygen and the energy released is stored in the bonds of energy storage compounds such as ATP. In fact, ATP drives the *dark reactions* which convert CO_2 and hydrogen (from water) into glucose and other carbohydrates.

In the presence of a suitable catalyst, ATP releases energy by undergoing a three-step hydrolysis of the P–O bond of its triphosphate groups. In the first step, ATP is hydrolysed to ADP and releases 31kJ mol^{-1} Gibbs energy. In the second step, ADP is converted into AMP (adenosine monophosphate) and produces approximately the same amount of energy. In the last step of the hydrolysis of AMP to adenosine, only 14 kJ mol^{-1} Gibb's energy is released.

The living plants may convert the glucose produced during photosynthesis into disaccharides, polysaccharides, starches, cellulose, proteins or oils. The end product depends on the type of plants involved and complexity of its biochemistry. Plants thus, are primary source of energy for animals and humans. This can be represented by oxidation of glucose which is reverse of photosynthesis.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O;\quad \Delta G^\circ = -2880 \text{ kJ mol}^{-1}$$

Part of the energy is utilized while a part of it is stored leading to the next reaction:

$$C_6H_{12}O_6 + 36\,ADP + 36\,H_3PO_4 + 6O_2 \rightarrow 6CO_2 + 36\,ATP + 42H_2O$$

We now take up the chemistry of important biomolecules.

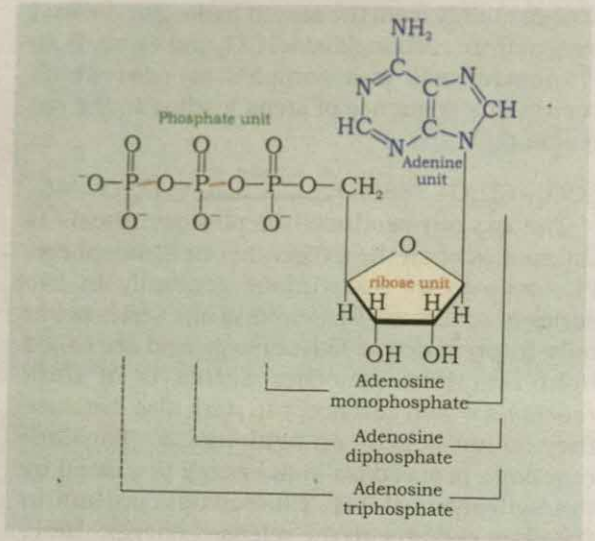


Fig. 17.2 *The high energy phosphate bonds of ATP are indicated by red colour. After hydrolysis a large amount of energy is released. All the constituent units (viz phosphate, ribose and adenine) are also indicated.*

17.2 CARBOHYDRATES

Carbohydrates have the general formula $C_x(H_2O)_y$. These can be described as optically active polyhydroxy aldehydes or ketones or the compounds which yield them on hydrolysis. Carbohydrates are also known as **saccharides**. They are the ultimate source of most of our food. We clothe ourselves with cellulose in the form of cotton, linen and rayon. We build furniture and houses from cellulose in the form of wood. Thus, carbohydrates provide us with basic necessities of life, food, clothing and shelter.

17.2.1 Classification

The carbohydrates can be divided into three major classes, depending upon whether they undergo hydrolysis, and if so, on the number of products formed.

(i) Monosaccharides: These cannot be hydrolysed to simpler compounds. Depending upon the total number of carbon atoms in monosaccharides and aldehyde or ketone functional groups present, the terms used for their classification are given in Table 17.1.

(ii) Oligosaccharides: The oligosaccharides (Greek, *oligo*, few) are carbohydrates which yield a few but definite number (2-10) of monosaccharide molecules on hydrolysis.

Table 17.1 Different types of monosaccharides

Carbon atoms	General terms	Aldehydes	Ketones
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

For example, a disaccharide on hydrolysis yields two monosaccharide molecules

$$\underset{\text{(Sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

A trisaccharide like raffinose on hydrolysis gives glucose, fructose and galactose.

(iii) Polysaccharides: These are high molecular mass carbohydrates which yield many molecules of monosaccharides on hydrolysis. Examples are starch and cellulose, both having general formula $(C_6H_{10}O_5)_n$.

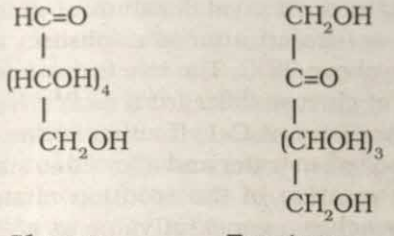
$$\underset{\text{Starch or cellulose}}{(C_6H_{10}O_5)_n} + n\,H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{n\,C_6H_{12}O_6}$$

In general monosaccharides and oligosaccharides are crystalline solids, soluble in water and sweet in taste. These are collectively known as **sugars**. The polysaccharides, on the other hand are amorphous, insoluble in water and tasteless and are known as **non-sugars**.

The carbohydrates may also be classified as either reducing or non-reducing sugars. All those carbohydrates which contain free aldehydic or ketonic group and reduce Fehling's solution and Tollen's reagent are referred to as reducing sugars. All monosaccharides whether aldose or ketose are *reducing sugars*. In disaccharides if the reducing groups of monosaccharides i.e., aldehydic or ketonic groups are bonded, these are non-reducing sugars e.g. sucrose, while others in which these functional groups are free, are reducing sugars e.g. maltose and lactose.

17.2.2 Monosaccharides

All carbohydrates are either monosaccharides or get converted to monosaccharides on hydrolysis. Glucose and fructose are the specific examples of an aldohexose and of a ketohexose respectively. These can be represented by the following formulae.



Glucose **Fructose**

17.2.3 Glucose (Dextrose; Grape sugar) $C_6H_{12}O_6$

Glucose occurs in nature in free as well as in the combined form. It is present in sweet fruits and honey. Ripe grapes contain ~ 20 % of glucose.

Preparation of Glucose

1. From Sucrose (Cane sugar): If sucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts,

$$\underset{\text{(Sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

2. From Starch: Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute H_2SO_4 at 393 K under pressure,

$$\underset{\text{Starch or cellulose}}{(C_6H_{12}O_5)_n} + n\,H_2O \xrightarrow[\text{393 K; 2-3 bar}]{H^+} \underset{\text{Glucose}}{n\,C_6H_{12}O_6}$$

17.2.4 Properties of Glucose

Glucose has one aldehyde group, one primary (–CH_2OH) and four secondary (–CHOH) hydroxyl groups and gives the following reactions;

1. Acetylation of glucose with acetic anhydride gives glucose pentaacetate confirming the presence of five hydroxyl groups in glucose.

$$OHC\text{-}(CHOH)_4\text{–}CH_2OH \xrightarrow{(CH_3CO)_2O} OHC\text{–}(CHOCOCH_3)_4\text{-}CH_2OOCCH_3$$

2. Glucose reacts with hydroxylamine to give monoxime and adds a molecule of hydrogen cyanide to give a cyanohydrin.

$$HOH_2C\text{-}(CHOH)_4\text{-}CHO + HONH_2 \longrightarrow \underset{\text{Glucose monoxime}}{HOCH_2\text{-}(CHOH)_4\text{-}CH{=}NOH}$$

$$HOCH_2\text{-}(CHOH)_4\text{-}CHO + HCN \longrightarrow \underset{\text{Glucose cyanohydrin}}{HOCH_2\text{-}(CHOH)_4\text{-}CH\,(OH)CN}$$

These reactions confirm the presence of a carbonyl group in glucose.

3. Glucose reduces ammoniacal silver nitrate solution (Tollen's reagent) to metallic silver and also Fehling's solution to reddish brown cuprous oxide and itself gets oxidized to gluconic acid. This confirms the presence of an aldehydic group in glucose.

$$HOCH_2\text{-}(CHOH)_4\text{-}CHO + Ag_2O \longrightarrow \underset{\text{Gluconic acid}}{HOCH_2\text{-}(CHOH)_4\text{-}COOH} + 2\,Ag$$

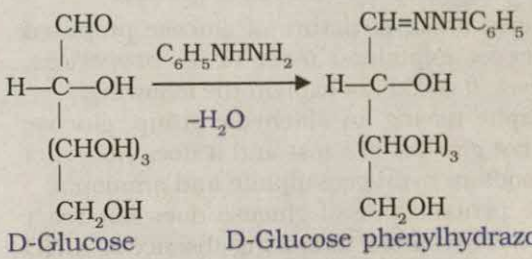
4. On oxidation with nitric acid glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid This indicates the presence of a primary alcoholic group in glucose.

$$HOCH_2\text{-}(CHOH)_4\text{-}CHO \xrightarrow{HNO_3} \underset{\text{Saccharic acid}}{HOOC\text{-}(CHOH)_4\text{-}COOH}$$

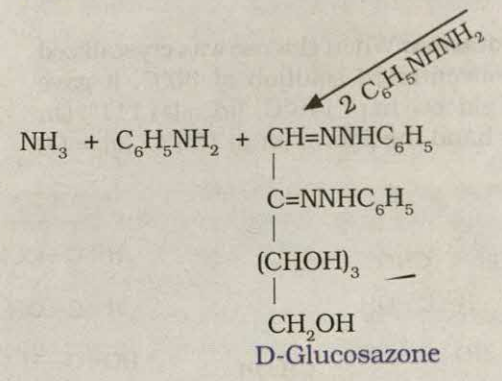
5. Glucose on prolonged heating with HI forms n- hexane, suggesting that all the 6 carbon atoms in glucose are linked linearly.

$$HOCH_2\text{-}(CHOH)_4\text{-}CHO \xrightarrow{HI} \underset{\text{n-hexane}}{H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3}$$

6. D-Glucose reacts with phenyl hydrazine to give glucose phenylhydrazone. If excess of phenylhydrazine is used, a dihydrazone, known as *osazone* is obtained which is called glucosazone.



D-Glucose D-Glucose phenylhydrazone



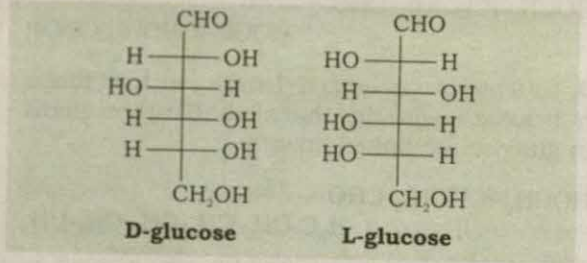
D-Glucosazone

7. On heating with conc. solution of sodium hydroxide glucose first turns yellow, then brown and finally resinifies. However, with dilute sodium hydroxide glucose undergoes a reversible isomerization and is converted into a mixture of D-glucose, D-mannose and D-fructose. This

reaction is known as *Lobry de Bruyn-van Ekenstein rearrangement*. Same results are obtained if mannose or fructose are treated with alkali. It is probably on account of this isomerization that fructose reduces Fehling's and Tollen's reagents in alkaline medium although it does not contain a –CHO group.

D-glucose $\rightleftharpoons$ D-mannose $\rightleftharpoons$ D-fructose

Glucose has been assigned a straight chain structure. The Fischer projections for D- and L-glucose are shown below:



D-glucose **L-glucose**

The stereochemistry of all sugars has been determined by relating it to that of D- or L- glyceraldehydes (Unit 12).

17.2.5 Cyclic Structure of D-glucose

The open chain structure of glucose proposed by Baeyer explained most of its properties. However, it could not explain the following.

1. Despite having an aldehydic group, glucose does not give Schiff's test and it does not react with sodium hydrogensulphite and ammonia.

2. The pentaacetate of glucose does not react with hydroxylamine indicating absence of –CHO group.

3. Mutarotation: When glucose was crystallized from a concentrated solution at 30°C, it gave α-form of glucose m.p. 146°C, $[\alpha]_D$= (+) 111°. On the other hand the β form (m.p. 150°C) $[\alpha]_D$= (+) 19.2° is obtained on crystallization of glucose from a hot saturated aqueous solution at a temperature above 98°C. The two forms known as *anomers* of glucose differ from each other in the stereochemistry at C-1. If either of the two forms is dissolved in water and allowed to stand, the specific rotation of the solution changes slowly and reaches a constant value at +52.5°. This equilibrium is reached faster if a trace of acid or base catalyst is present.

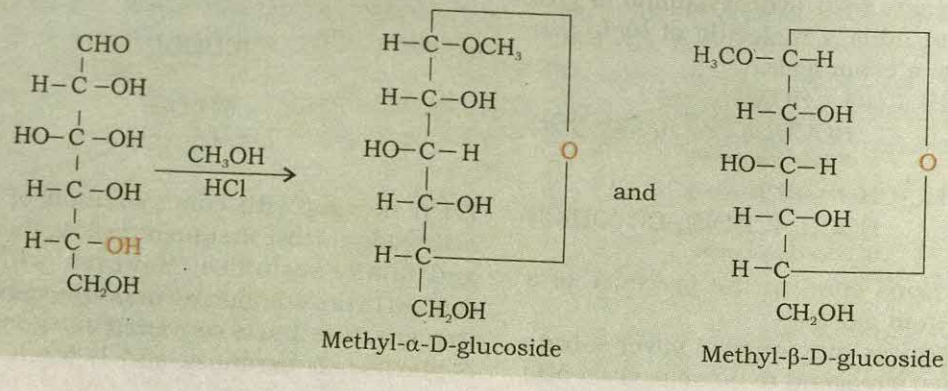
The spontaneous change in specific rotation of an optically active compound is called mutarotation.

4. When glucose is treated with methanol in the presence of dry hydrogen chloride gas, it yields two isomeric monomethyl derivatives known as methyl α-D-glucoside and methyl β–D-glucoside. These glucosides do not reduce Fehling's solution and also do not react with hydrogen cyanide or hydroxylamine indicating the absence of a free –CHO group. Their formation can be shown as given below. (See Box)

By analogy to the formation of these two methyl glucosides, glucose exists in two forms α-D-glucose and β-D-glucose.

α-D- (+) glucose $\rightleftharpoons$ Equilibrium mixture + 52.5° $\rightleftharpoons$ β-D (+) glucose

As a result of cyclization, the anomeric carbon (C-1) becomes asymmetric and the newly formed –OH group may be either on the left or on right in Fischer projection, thus resulting in the formation of two isomers (anomers). The isomers having the hydroxyl group to the left of the C-1 is designated β-D-glucose and one having the hydroxyl group on the right as α-D-glucose.



Methyl-α-D-glucoside Methyl-β-D-glucoside

These two forms are not mirror images of each other, hence are not enantiomers. The six membered cyclic structure of glucose was established by R.D. Haworth. The six membered cyclic structure of glucose is called *pyranose structure* (α or β), in analogy with pyran, a six membered ring with one oxygen and five carbon atoms in the ring. The 5-membered ring structure of glucose is known as furanose in analogy with furan, a five membered ring with one oxygen and four carbons. However, glucose occurs in nature only in the pyranose form. (Fig. 17.3)

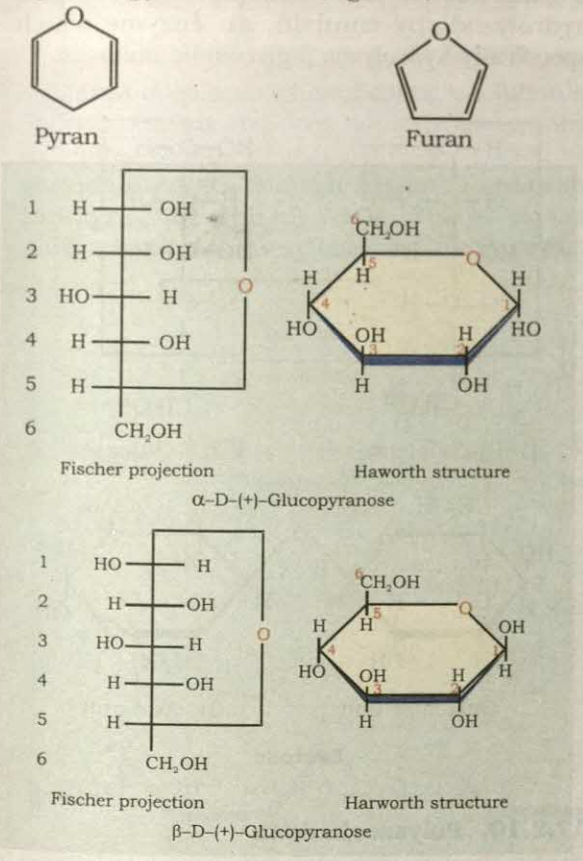


Fig. 17.3 *Fishcer projections and Haworth structures of α-D-(+)-Glucopyranose.*

The lower thickened edge of the ring in Haworth structure is nearest to the observer. The groups projected to the right in Fischer projection are written below the plane of the ring in Haworth structure and those on the left are written above the plane of the ring.

17.2.6 Disaccharides

The disaccharides are composed of two molecules of monosaccharides. On hydrolysis with dilute acids or enzymes they yield two molecules of either the same or different monosaccharides, e.g.,

$$C_{12}H_{22}O_{11} \xrightarrow[H^+]{H_2O} C_6H_{12}O_6 + C_6H_{12}O_6$$
Sucrose → Glucose + Fructose

$$C_{12}H_{22}O_{11} \xrightarrow[H^+]{H_2O} C_6H_{12}O_6 + C_6H_{12}O_6$$
Lactose → Glucose + Galactose

$$C_{12}H_{22}O_{11} \xrightarrow[H^+]{H_2O} C_6H_{12}O_6 + C_6H_{12}O_6$$
Maltose → Glucose + Glucose

The disaccharides may be reducing or nonreducing depending upon the position of linkages between the two monosaccharide units. *If this glycosidic linkage involves the carbonyl functions of both the monosacccharide units, the resulting disaccharide would be non-reducing e.g. sucrose. If one of the carbonyl functions in anyone of the monosaccharide unit is free, the resulting disaccharide would be reducing sugar, e.g., maltose and lactose.*

17.2.7 Sucrose / Cane sugar ($C_{12}H_{22}O_{11}$)

It is the most common disaccharide widely distributed in plants. It is manufactured either from sugarcane or beet root. It is a colourless, crystalline and sweet substance soluble in water. Its aqueous solution is dextrorotatory, $[\alpha]_D$= +66.5°. On hydrolysis with dilute acids or enzyme invertase, canesugar gives equimolar mixture of D- (+)- glucose and D-(-)-fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{HCl} \underset{\text{D-glucose}}{C_6H_{12}O_6} + \underset{\text{D-fructose}}{C_6H_{12}O_6}$$
$[\alpha]_D$ = + 66.5° → $[\alpha]_D$ = +52.5° + $[\alpha]_D$ = −92.4°

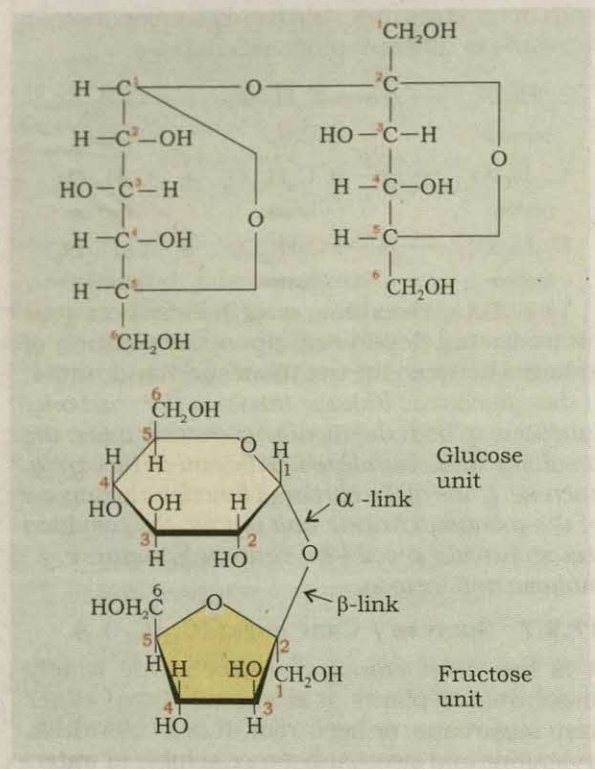
Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (-) and such a change is known as **inversion** and the mixture is known as *invert sugar.*

Sucrose solution is fermented by yeast when the enzyme invertase hydrolyses sucrose to glucose and fructose; enzyme, zymase converts these monosaccharides to ethyl alcohol.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose or fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

Haworth (1927) suggested the following structure for sucrose. As mentioned earlier it is a non-reducing sugar.

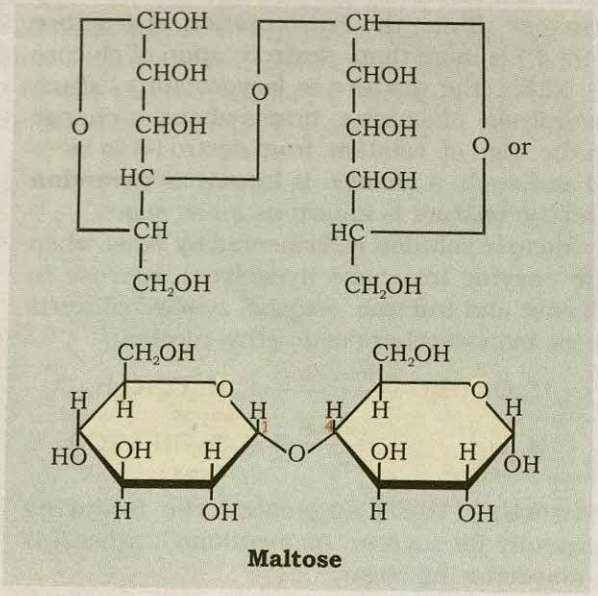


Haworth's representation of Sucrose

17.2.8 Maltose (Malt sugar, $C_{12}H_{22}O_{11}$)

It is obtained by partial hydrolysis of starch by diastase, an enzyme present in malt (sprouted barley seeds).

$$\underset{\text{Starch}}{2\,(C_6H_{10}O_5)_n} + n\,H_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{n\,C_{12}H_{22}O_{11}}$$

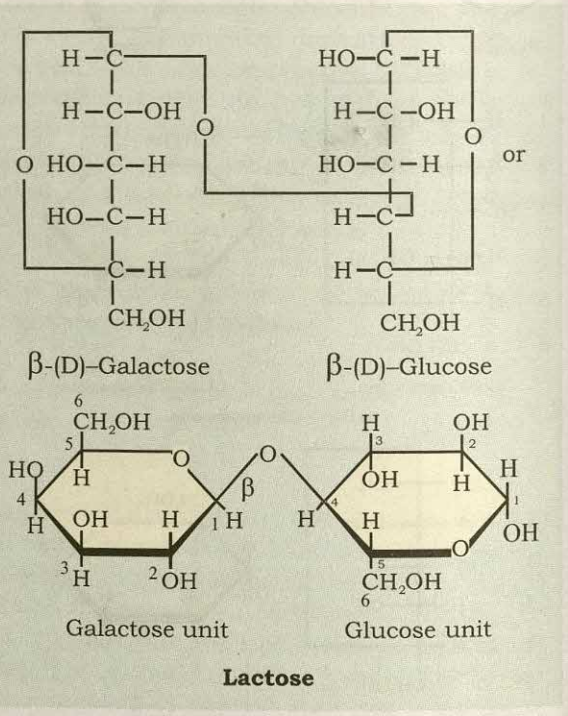


Maltose

On hydrolysis one mole of maltose yields two moles of D-glucose. It is a reducing sugar. The two glucose units are linked through a α-glycosidic linkage between C-1 of one unit and the C-4 of another. Both glucose units are in pyranose form.

17.2.9 Lactose ($C_{12}H_{22}O_{11}$)

Lactose occurs in milk and is also called milk sugar. Hydrolysis of lactose with dilute acid yields equimolar mixture of D-glucose and D-galactose. It is a reducing sugar. It gets hydrolysed by emulsin, an enzyme which specifically hydrolyses β-glycosidic linkages.



Lactose

17.2.10 Polysaccharides

These are carbohydrates in which hundreds or even thousands of monosaccharide units are joined together by glycosidic linkages. Some examples of polysaccharides are starch, cellulose, glycogen and dextrins. However, starch and cellulose are most important of the polysaccharides.

Starch / Amylum $(C_6H_{10}O_5)_n$: Starch occurs in all plants, particularly in their seeds. The main sources are wheat, maize, rice, potatoes, barley and sorghum. Starch occurs in the form of granules, which vary in size and shape depending on their plant source. Starch is a

white amorphous powder, insoluble in cold water. Its solution in water gives a blue colour with iodine solution. The blue colour disappears on heating and reappears on cooling. On hydrolysis with dilute acids or enzyme, starch breaks down to molecules of variable complexity (n> n´), maltose and finally D-glucose.

$$(C_6H_{10}O_5)_n \longrightarrow (C_6H_{10}O_5)_{n'} \longrightarrow C_{12}H_{22}O_{11}$$

Starch — Diastase — Maltose

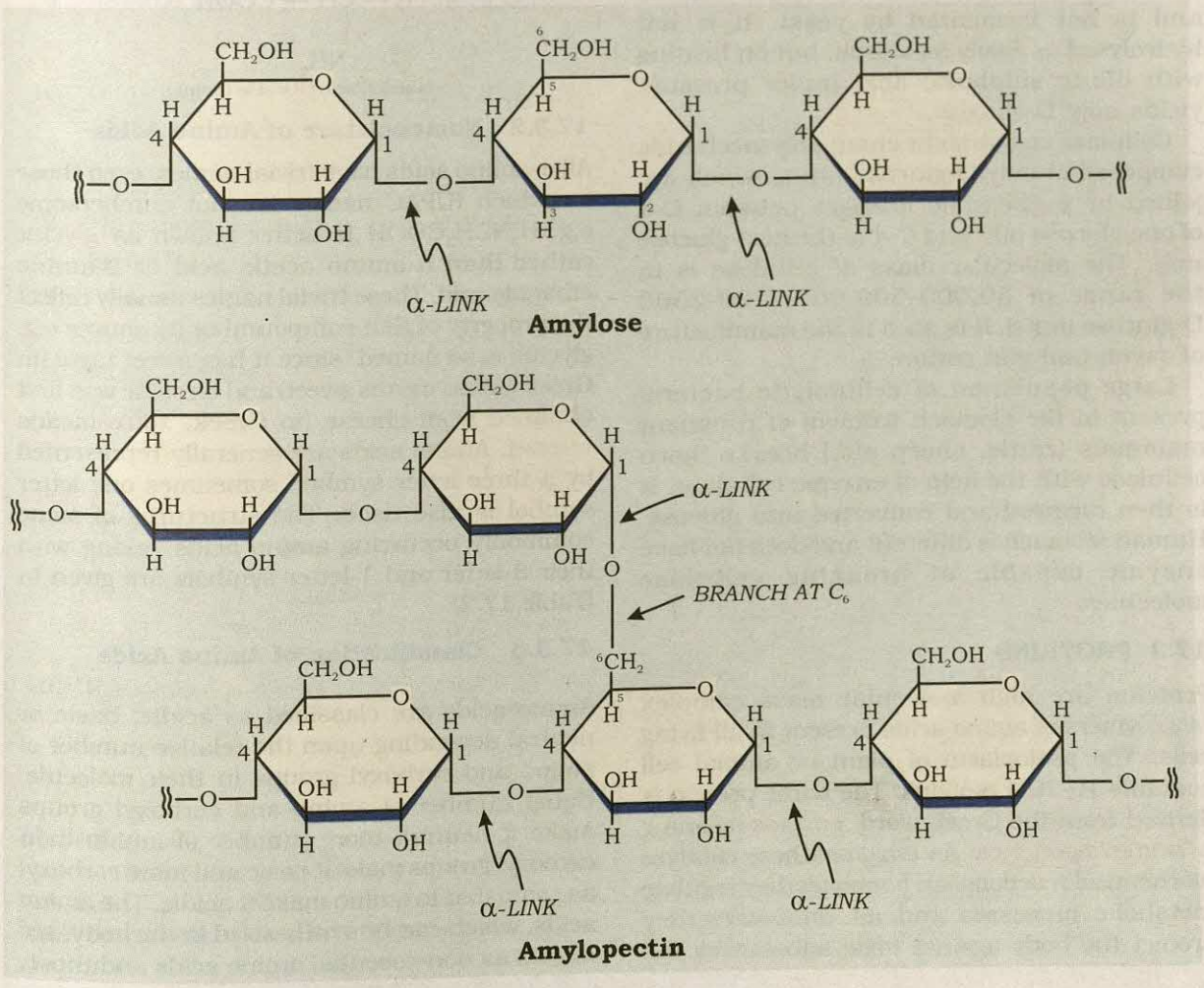
$$C_6H_{12}O_6$$

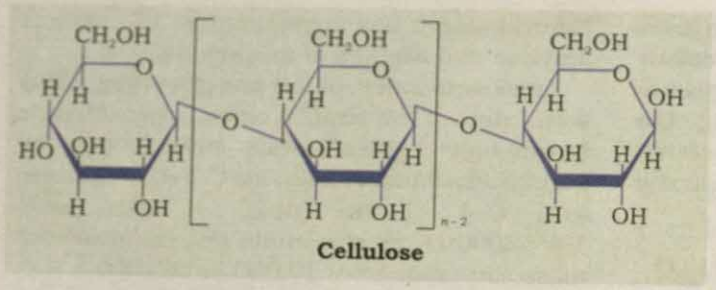
D-glucose

Starch does not reduce Fehling's solution or Tollen's reagent and does not form an osazone, indicating that all hemiacetal hydroxyl group of glucose units (C-1) are linked with glycosidic linkages. Starch is a mixture of two polysaccharides, amylose and amylopectin. Natural starch has approximately 10 - 20% of amylose and 80-90% of amylopectin.

Amylose is water soluble and gives blue colour with iodine. It is a straight chain polysaccharide having only D-glucose units joined together by α-glycosidic linkages involving C-1 of one glucose and C-4 of the next. It can have 100- 3000 D- glucose units i.e., its molecular mass can range from 10,000 to 500,000.

Amylopectin is a branched chain polysaccharide insoluble in water which does not give blue colour with iodine. It is composed of chains of 25-30 D-glucose units joined by α-D-glycosidic linkages between C-1 of one glucose unit and C-4 of the next glucose unit (similar to amylose). However, these chains are connected with each other by 1,6-linkages. Starch is a major food material for us. It is hydrolyzed by enzyme amylase present in saliva. The end product is glucose which is an essential nutrient.





Cellulose

Cellulose $(C_6H_{10}O_5)_n$: It is the chief constituent of the cell walls of plants. Wood contains 45-50% while cotton contains 90-95% cellulose. It is a colourless amorphous solid which decomposes on heating. It is largely linear and its individual strands align with each other through multiple hydrogen bonds. This lends rigidity to its structure. It is thus used effectively as a cell wall material.

Cellulose does not reduce Tollen's reagent or Fehling's solution. It does not form osazone and is not fermented by yeast. It is not hydrolysed as easily as starch, but on heating with dilute sulphuric acid under pressure yields only D-glucose.

Cellulose is a straight chain polysaccharide composed of only D-glucose units, which are joined by β-glycosidic linkages between C-1 of one glucose unit and C-4 of the next glucose unit. The molecular mass of cellulose is in the range of 50,000-500,000 (300-2500 D-glucose units). It is used in the manufacture of rayon and gun cotton.

Large population of cellulolytic bacteria present in the stomach (rumen) of ruminant mammals (cattle, sheep etc.) breaks down cellulose with the help of enzyme cellulase. It is then digested and converted into glucose. Human stomach is different and does not have enzyme capable of breaking cellulose molecules.

17.3 PROTEINS

Proteins are high molecular mass complex biopolymers of amino acids present in all living cells. The protoplasm of plant or animal cell contains 10-20% proteins. The name protein is derived from the Greek word *proteios* meaning *of prime importance*. As *enzymes* these catalyze biochemical reactions, as *hormones* they regulate metabolic processes and as *antibodies* they protect the body against toxic substances. All proteins contain the elements carbon, hydrogen, oxygen, nitrogen and sulphur. Some of these may also contain phosphorus, iodine and traces of metals like iron, copper, zinc and manganese. All proteins on partial hydrolysis give peptides of varying molecular masses which on complete hydrolysis give amino acids.

$$\text{Proteins} \xrightarrow{\text{Hydrolysis}} \text{Peptides} \xrightarrow{\text{Hydrolysis}} \text{Amino acids}$$

17.3.1 Amino Acids

Amino acids contain amino (-NH_2) and carboxyl (-COOH) functional groups. Depending upon the relative position of the two functional groups in the alkyl chain the amino acids can be classified as α, β, γ, δ and so on. Only α-amino acids are obtained on hydrolysis of proteins. These may contain other functional groups also.

$$\begin{array}{l} R-\underset{|}{\overset{|}{CH}}-COOH \\ \quad\quad NH_2 \end{array}$$

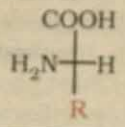
α-amino acid (R = side chain)

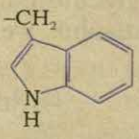
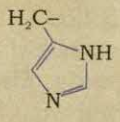
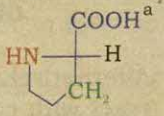
17.3.2 Nomenclature of Amino Acids

All α-amino acids have trivial names, even those for which IUPAC names are not cumbersome e.g. H_2NCH_2COOH is better known as glycine rather than α-amino acetic acid or 2-amino ethanoic acid. These trivial names usually reflect the property of that compound or its source e.g. glycine is so named since it has sweet taste (in Greek *glykos* means sweet) and tyrosine was first obtained from cheese (in Greek, *tyros* means cheese). Amino acids are generally represented by a three letter symbol, sometimes one letter symbol is also used. The structures of some commonly occurring amino acids along with their 3-letter and 1-letter symbols are given in (Table 17.2).

17.3.3 Classification of Amino Acids

Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule. Equal number of amino and carboxyl groups make it neutral, more number of amino than carboxyl groups make it basic and more carboxyl as compared to amino make it acidic. The amino acids, which can be synthesized in the body, are known as non-essential amino acids and those,

Table 17.2 Natural Amino Acids, 

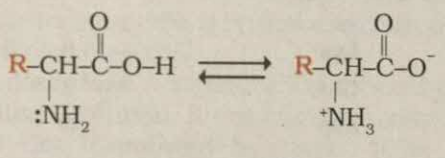
Name of the amino acids	Characteristic feature of side chain, R	Three letter symbol	One letter code
1. Glycine	H	Gly	G
2. Alanine	$-CH_3$	Ala	A
3. Valine*	$(H_3C)_2CH-$	Val	V
4. Leucine*	$(H_3C)_2CH-CH_2-$	Leu	L
5. Isoleucine*	$H_3C-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-$	Ile	I
6. Arginine*	$HN=\underset{\displaystyle NH_2}{\underset{\vert}{C}}-NH-(CH_2)_3-$	Arg	R
7. Lysine*	$H_2N-(CH_2)_4-$	Lys	K
8. Glutamic acid	$HOOC-CH_2-CH_2-$	Glu	E
9. Aspartic acid	$HOOC-CH_2-$	Asp	D
10. Glutamine	$H_2N-\overset{\displaystyle O}{\overset{\Vert}{C}}-CH_2-CH_2-$	Gln	Q
11. Asparagine	$H_2N-\overset{\displaystyle O}{\overset{\Vert}{C}}-CH_2-$	Asn	N
12. Threonine*	$H_3C-CHOH-$	Thr	T
13. Serine	$HO-CH_2-$	Ser	S
14. Cysteine	$HS-CH_2-$	Cys	C
15. Methionine*	$H_3C-S-CH_2-CH_2-$	Met	M
16. Phenylalanine*	$C_6H_5-CH_2-$	Phe	F
17. Tyrosine	$(p)HO-C_6H_4-CH_2-$	Tyr	Y
18. Tryptophan*		Trp	W
19. Histidine*		His	H
20. Proline		Pro	P

* essential amino acid , a = entire structure

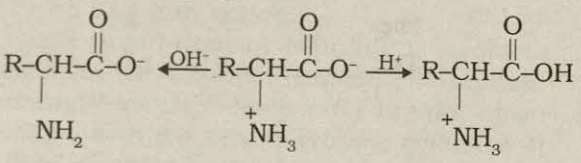
which cannot be synthesized in the body but must be obtained through diet, are known as essential amino acids (marked in Table 17.2).

17.3.4 Physical Properties of α-Amino Acids

Amino acids are usually colourless, crystalline solids. These are water-soluble high melting solids and behave like salts rather than simple amines or carboxylic acids. This behavior is due to the presence of both an acidic (carboxyl group) and a basic (amino group) group in the same molecule. In aqueous solution the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as **zwitter ion**. This is neutral but contains both positive and negative charges.



In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases. In acidic solution, the carboxylate function ($-COO^-$) accepts a proton and gets converted to carboxyl substituent (-COOH), while in basic solution the ammonium substituent $\left(\overset{+}{N}H_3\right)$ changes to amino group ($-NH_2$) by losing a proton.



In acidic solution, an amino acid exists as a positive ion and migrates towards the cathode in an electric field, while in alkaline solution it exists as a negative ion and migrates towards anode. At a certain hydrogen ion concentration (pH), the dipolar ion exists as a neutral ion and does not migrate to either electrode. This pH is known as the **isoelectric point** of the amino acid. The isoelectric point depends on other functional groups in the amino acid, and neutral amino acids have isoelectric points in the range of pH 5.5 to 6.3. At isoelectric point the amino acids have least solubility in water and this property is exploited in the separation of different amino acids obtained from the hydrolysis of proteins.

Except glycine, all other naturally occurring α-amino acids are optically active, since the α-carbon atom is asymmetric. These exist both in 'D' and 'L' forms. Their Fischer projection formulae are written with carboxyl group (-COOH) at the top. In the 'D' form amino group ($-NH_2$) is written on the right side and in the 'L' form on the left side. This is similar to the placement of hydroxyl group (-OH) in glyceraldehydes, the reference compound for carbohydrates (Unit 12).

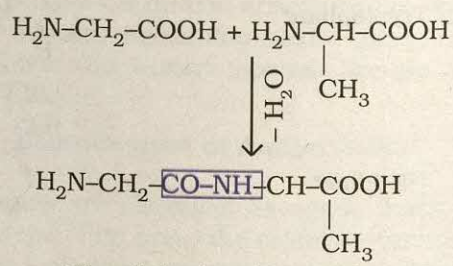
'D' and 'L' refer to the configuration of the amino acid molecule about the asymmetric carbon atom. Most naturally occurring amino acids have L-configuration.

17.3.5 Chemical Properties of α- Amino Acids

Amino acids form salts with acids as well as with bases. Their chemical reactions are similar to primary amines and carboxylic acids (Units 14 and 15).

17.3.6 Peptides

We have learnt earlier in this unit that proteins on hydrolysis break down into smaller fragments called peptides which finally give α - amino acids, **The peptide bond:** The reaction between two molecules of the same or different amino acids, proceed through the combination of the amino group of one molecule with the carboxyl group of the other. This results in the elimination of a water molecule and formation of a peptide bond –CO–NH–. For example, when carboxyl group of glycine combines with the amino group of alanine, we get, glycylalanine.



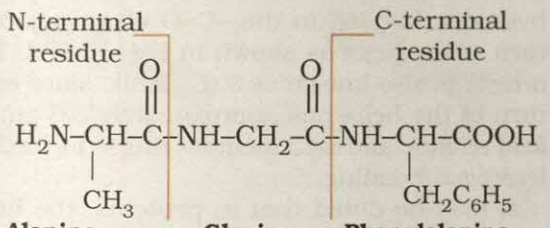
Glycylalanine (Gly-Ala)

Alternatively the amino group of glycine may react with carboxyl group of alanine, resulting in the formation of a different dipeptide, alanylglycine (Ala - Gly).

In both the dipeptides i.e., glycylalanine or alanylglycine, there are free functional groups at both ends. These groups can further react with the relevant groups of the other amino acids forming tri, tetra, penta peptides and so on.

17.3.7 Polypeptides

As a matter of convention the structure of polypeptides is written in a way that the amino acid with the free amino ($-NH_2$) group known as N-terminal residue is written on the left hand side of the polypeptide chain and the amino acid with the free carboxyl group (C- terminal residue) is written on the right hand side of the chain. Thus, a tripeptide, **alanylglycylphenylalanine** is represented as follows,



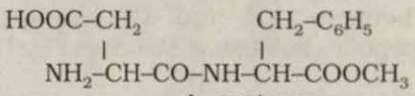
Ala – Gly – Phe

The name of any polypeptide is written starting from the N-terminal residue. The suffix-**ine** in the name of the amino acid is replaced by – **yl** (as glycine to glycyl, alanine to alanyl etc.) for all amino acids except the C- terminal acid. This nomenclature is not used frequently. Instead, the three letter or one letter abbreviation for the amino acid (as given in Table 17.2) is used e.g. the above tripeptide is named as Ala-Gly-Phe or A-G-F.

Relatively shorter peptides are known as **oligopeptides** whereas longer polymers are called **polypeptides**. A polypeptide with more than hundred or so amino acid residues, having molecular mass higher than 10,000 is called a protein. However, the distinction between a polypeptide and a protein is not sharp. Polypeptides with fewer amino acids are likely to be called proteins if they ordinarily have a well-defined conformation of a protein (Section 17.3.9).

Polypeptides are amphoteric because of the presence of terminal ammonium and carboxylate ions as well as the ionized side chains of amino acid residues. Therefore, they titrate as acids or bases and have an isoelectric point at which they are frequently least soluble and have the greatest tendency to aggregate.

The functions of proteins are important and varied in bio-systems, however, the smaller peptides also have important functions though their total content in tissues is small compared to proteins. Some of these are very potent. Most of the toxins (poisonous substances) in animal venoms and in plant sources are polypeptides. Minute amount of some oligopeptides with as few as three modified amino acid residues are effective as hormones. A derivative of dipeptide, aspartylphenylalanine methyl ester (aspartame) is 160 times as sweet as sucrose and is used as a sugar substitute.



Aspartame

Example 17.1
A tripeptide on complete hydrolysis gives glycine, alanine and phenylalanine. Using three letter symbols write down the possible sequences of the tripeptide.

Solution The possible combinations can be,

(i) Gly-Ala-Phe (ii) Gly-Phe-Ala
(iii) Ala-Gly-Phe (iv) Ala-Phe-Gly
(v) Phe-Gly-Ala (vi) Phe-Ala-Gly

17.3.8 Structure of Proteins

Proteins are considered to be biopolymers containing a large number of amino acids joined to each other by peptide linkages having three dimensional (3 D) structures. Protein structure and shape can be studied at four different levels, i.e., primary, secondary, tertiary and quaternary structures, each level being more complex than the previous one.

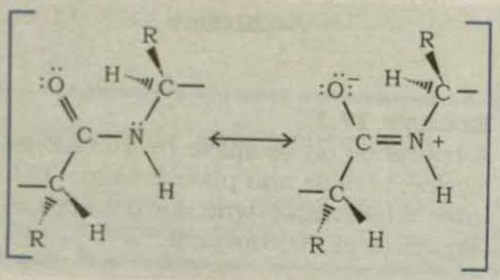
17.3.9 Primary Structure of Protein

Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of that protein. Any change in this primary structure i.e., the sequence of amino acids creates a different protein.

A protein containing a total of 100 amino acid residues is a very small protein, yet 20 different amino acids can be combined at one time in $(20)^{100}$ different ways.

17.3.10 Secondary Structure

The secondary structure of a protein refers to the shape in which a long polypeptide chain can exist. There are two different conformations of the peptide linkage present in proteins viz. α-helix and β-conformation. The α-helix model postulated by Linus Pauling in 1951 purely on theoretical considerations was later verified experimentally. In order to understand this, let us look at the nature of the peptide bond, which shows resonance as shown below. Hydrogen bonding between –NH- and –C=O groups on different peptides linkages is shown in Fig. 17.5.



Resonance Structure of Amide Linkage

Due to the partial double bond character of the C-N bond in peptide linkage, the amide part i.e., –CO-NH- is planar and rigid i.e., no free rotation about this bond is possible. As shown in Fig. 17.4, the free rotation of a peptide chain can only occur around the bonds joining the nearly planar amide groups to the α-carbons. The angles shown as Φ and Ψ in the figure are known as Ramachandran angles after the name of the Indian Biophysicist, G.N.A. Ramachandran. Note that C=O and -NH groups of the peptide bond are trans to each other.

Hydrogen bonds between –N-H and –C=O groups of peptide bonds give stability to the structure. Thus, a structure having maximum hydrogen bonds shall be favoured. α-Helix is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw (helix) with the –NH group of each amino acid residue hydrogen bonded to the –C=O of an adjacent turn of the helix as shown in Fig. 17.5(b). The α-helix is also known as 3.6_{13} helix, since each turn of the helix has approximately 3.6 amino acid residue and a 13 member ring is formed by hydrogen bonding.

It may be noted that in proteins, the helix always has a right handed arrangement. If you hold your hand so that the thumb points in the direction of travel along the axis of the helix, the curl of your fingers describes the direction in which the helix rotates, Fig. 17.5(a). All amino acids in a polypeptide chain have L-configuration and therefore, it can only result in a stable helix if it is right handed. The ball and stick model of a α-helix present is shown in Fig. 17.5(c).

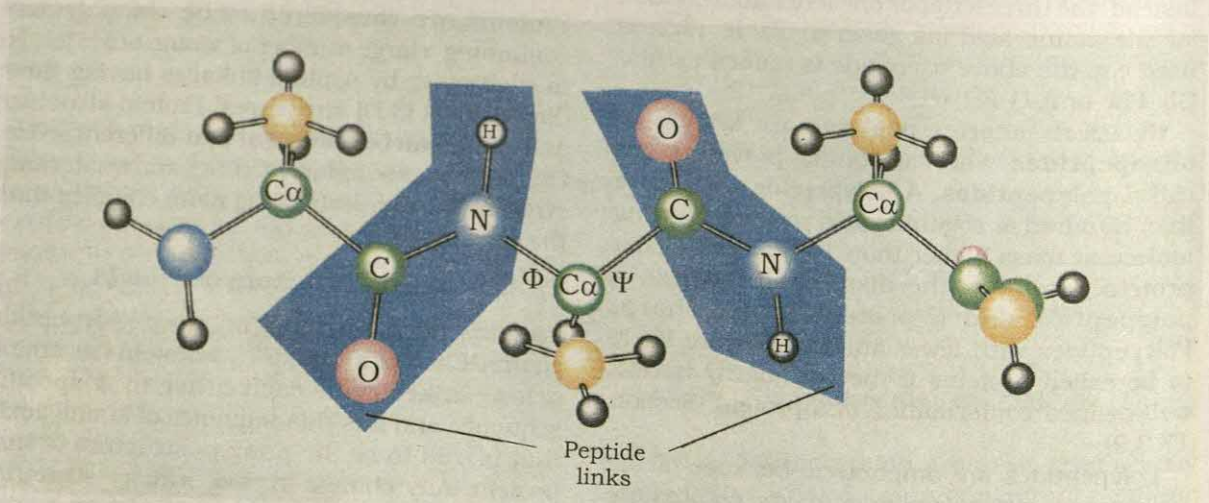


Fig. 17.4 *Model of a tripeptide showing peptide bonds in boxes and Ramchandran angles of rotation (Φ and Ψ) around α-carbon.*

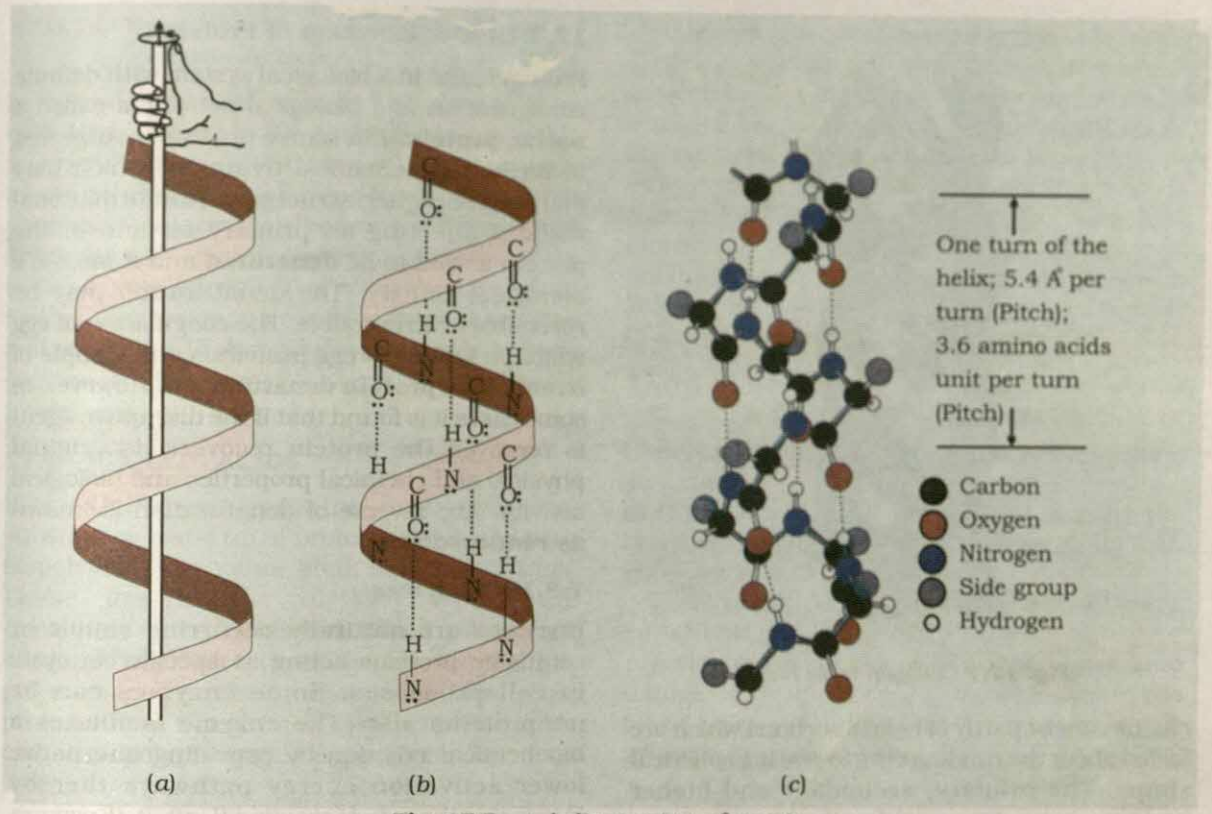


Fig. 17.5 *α - helix structure of protein.*

β- Structure was also proposed by Linus Pauling and co-workers in 1951. In this conformation all peptide chains are stretched out to nearly maximum extension and then laid side by side, held together by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as β-pleated sheet. The polypeptide chains may run parallel i.e. in the same direction or may be antiparallel i.e. run in opposite directions (Fig.17.6). N-termini are aligned head to head i.e., on the same side in parallel β-conformation and are aligned head to tail i.e., N-terminus of one chain and C-terminus of another chain are on the same side in antiparallel conformation. The β-sheet is parallel in keratin, the protein present in hair and antiparallel in silk fibroin.

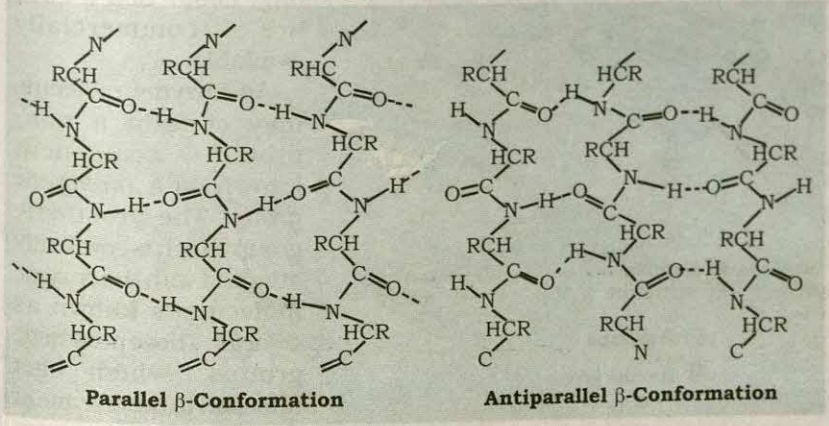


Fig. 17.6 *β - sheet of proteins.*

17.3.11 Tertiary Structure of Proteins

The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. Two major molecular shapes are found viz. fibrous and globular. The fibrous proteins e.g. silk, collagen and α-keratins have large helical content and have rod like rigid shape and are insoluble in water. The structure of collagen triple helix is shown in Fig. 17.7. In globular proteins e.g., haemoglobin the polypeptide

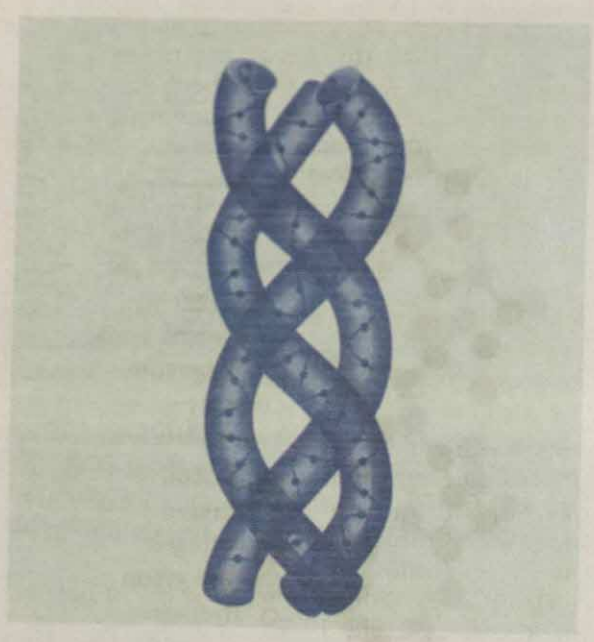


Fig. 17.7 Collagen triple helix

chains consist partly of helical sections which are folded about the random cuts to give it a spherical shape. The primary, secondary and higher (tertiary and quaternary) levels of heamoglobin structure are given in Fig. 17.8.

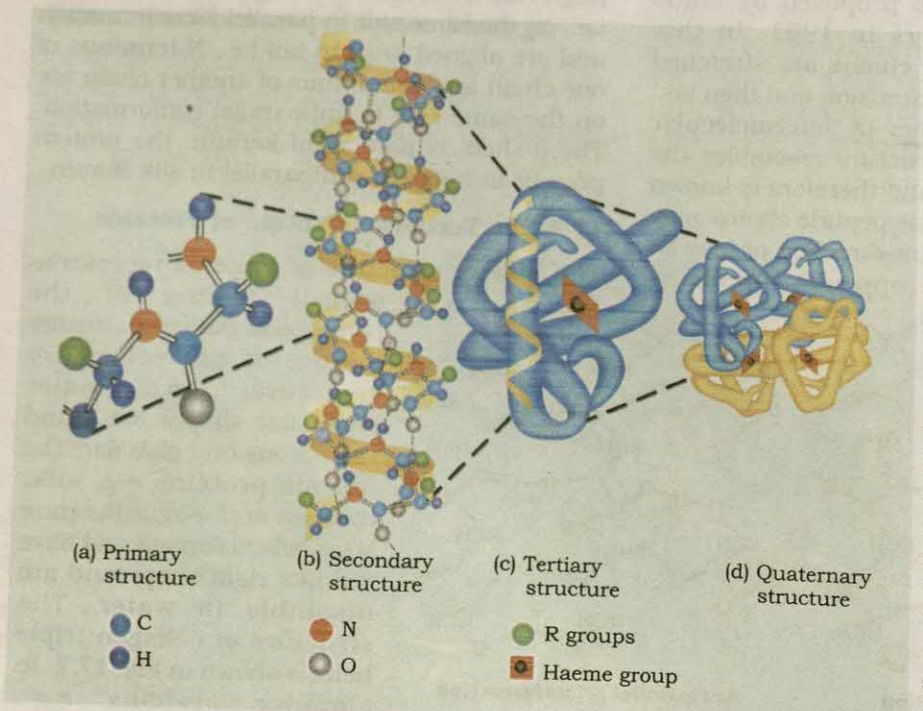


Fig. 17.8 Primary, secondary, teritiary and quaternary structures of haemoglobin.

17.3.12 Denaturation of Proteins

Protein found in a biological system with definite configuration and biological activity is called a **native protein**. If a native protein is subjected to physical or chemical treatment which may disrupt its higher structures (conformations) without affecting its primary structure, the protein is said to be **denatured** and it loses it's biological activity. The denaturation may be reversible or irreversible. The coagulation of egg white on boiling of egg protein is an example of **irreversible protein denaturation**. However, in some cases it is found that if the disruptive agent is removed the protein recovers its original physical and chemical properties and biological activity. The reverse of denaturation is known as ***renaturation***.

7.3.13 Enzymes

Enzymes are naturally occurring simple or conjugate proteins acting as specific catalysts in cell processes. Some enzymes can be nonproteins also. The enzyme facilitates a biochemical reaction by providing alternative lower activation energy pathways thereby increasing the rate of reaction (Unit 7). (Enzymes being proteins have colloidal nature and often get inactivated during reactions and have to be constantly replaced by synthesis in the body.)

At present about 3000 enzymes have been recognized by the International Union of Biochemistry. However, only about 300 (~10%) are commercially available.

An enzyme molecule may contain a non-protein component known as a *prosthetic group*. The prosthetic group which is covalently attached with the enzyme molecule is known as *cofactor*. Those prosthetic groups which get attached to the enzyme at the time of reaction are known as *coenzymes*.

17.3.14 Specificity and Mechanism of Enzyme Action

In case of enzymatic reaction the enzyme is so built that it binds to the substrate in a specific manner (Unit 7). The enzymatic reaction may proceed through the following four stages, (i) the formation of complex between enzyme and substrate (ES), (ii) the conversion of this complex to an enzyme-intermediate complex (EI) and (iii) further conversion to a complex between enzyme and product (EP) and (iv) the dissociation of the enzyme-product complex, leaving the enzyme unchanged.

17.4 NUCLEIC ACIDS

Every living cell contains *nucleoproteins*, substances made up of proteins combined with biopolymers of another kind, the *nucleic acids*. These are mainly of two types, the *deoxyribonucleic acids (DNA)* and *ribonucleic acids (RNA)*. Nucleic acids are long chain polymers (polynucleotides) of *nucleotides*. While proteins have a polyamide chain, nucleic acids contain a polyphosphate ester chain.

In higher cells, DNA is localized mainly in the nucleus, within the chromosome. A small amount of DNA is present in the cytoplasm also where it is contained in mitochondria and chloroplasts. RNA is also present in nucleus as well as cytoplasm. DNA is the major source of genetic information, which is copied into RNA molecules (*transcription*). The sequence of nucleotides contains the' **Code** for specific amino acid sequences. Proteins are then synthesized in a process involving *translation* of RNA.

17.4.1 Chemical Composition of Nucleic Acid (Primary Structure)

Complete hydrolysis of DNA (or RNA) yields a pentose sugar (ribose in RNA and deoxyribose in DNA), two types of heterocyclic nitrogenous bases viz., purines and pyrimidines along with phosphoric acid.

Deoxyribose differs from ribose in not having an –OH on C–2 (Fig. 17.9).

As shown in the figure the pyrimidines have a single heterocyclic ring while purines have two fused rings. DNA contains the purine bases, adenine (A) and guanine (G), and pyrimidine

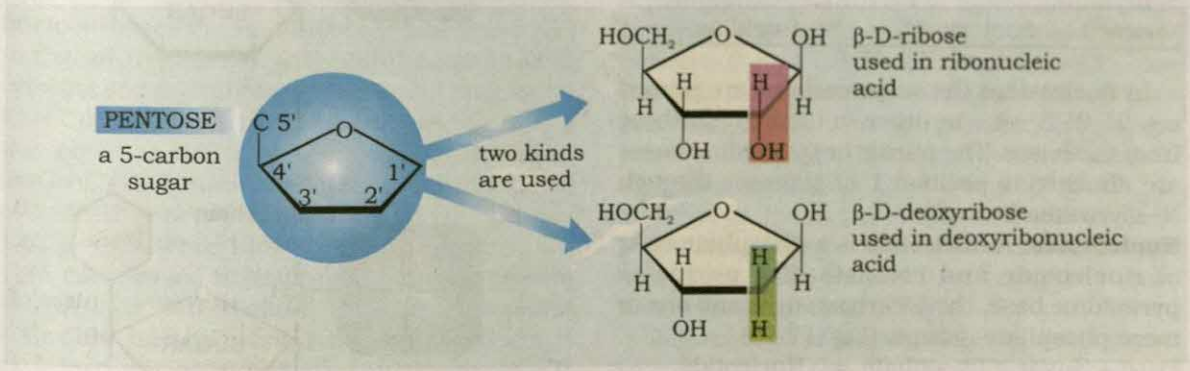


Fig. 17.9 *Structure of β -D-ribose and β -D-deoxyribose.*

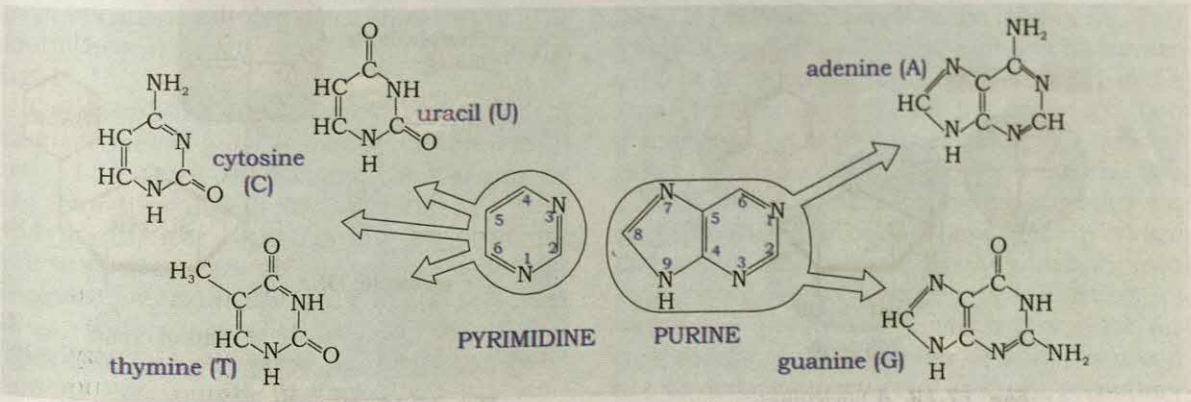


Fig. 17.10 *Purine and Pyrimidine Bases.*

bases, thymine (T) and cytosine (C) while RNA has uracil (U) in place of thymine (T). It can be noted that there are two main structural differences between DNA and RNA; (1) DNA has deoxyribose while RNA has ribose sugar, (2) DNA contains thymine while RNA has uracil.

Nucleosides: The N- glycosides of purine or pyrimidine bases with pentose sugars are known as nucleosides:

Base + Sugar = Nucleoside (Fig. 17.11).

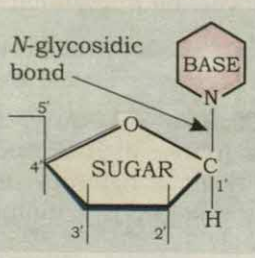


Fig. 17.11 *Base-Sugar linkage.*

Base	Abbreviation	Nucleoside
adenine	A	adenosine
guanine	G	guanosine
cytosine	C	cytidine
thymine	T	thymidine
uracil	U	uridine

In nucleosides the sugar carbons are primed e.g. 1′, 2′, 3′, etc. in order to distinguish these from the bases. The purine or pyrimidine bases are attached to position 1′ of pentoses through N- glycosidic linkages.

Nucleotides: A nucleotide is a phosphate ester of nucleoside and consists of a purine or pyrimidine base, the 5-carbon sugar and one or more phosphate groups. (Fig. 17.12)

Base + Sugar + Phosphate = Nucleotide

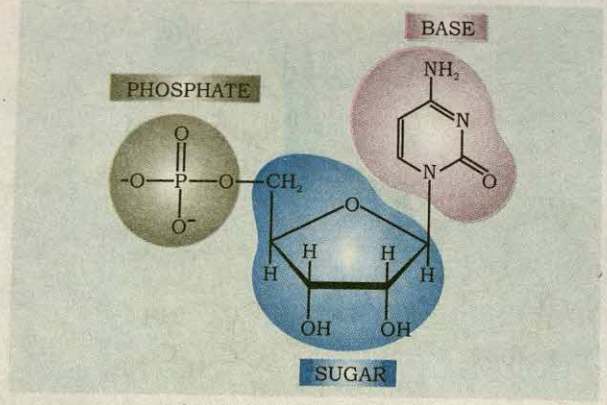


Fig. 17.12 *A nucleotide.*

The nucleotides are abbreviated by three capital letters, preceded by d- in case of deoxy series e.g.,

AMP = adenosine monophosphate

dAMP = deoxyadenosine monophosphate

ATP = adenosine triphosphate

UDP = uridine diphosphate etc.

Nucleotides are joined together by phosphodiester linkages between 5′ and 3′ carbon atoms of the pentose sugar. The formation of a typical dinucleotide is shown in Fig. 17.13.

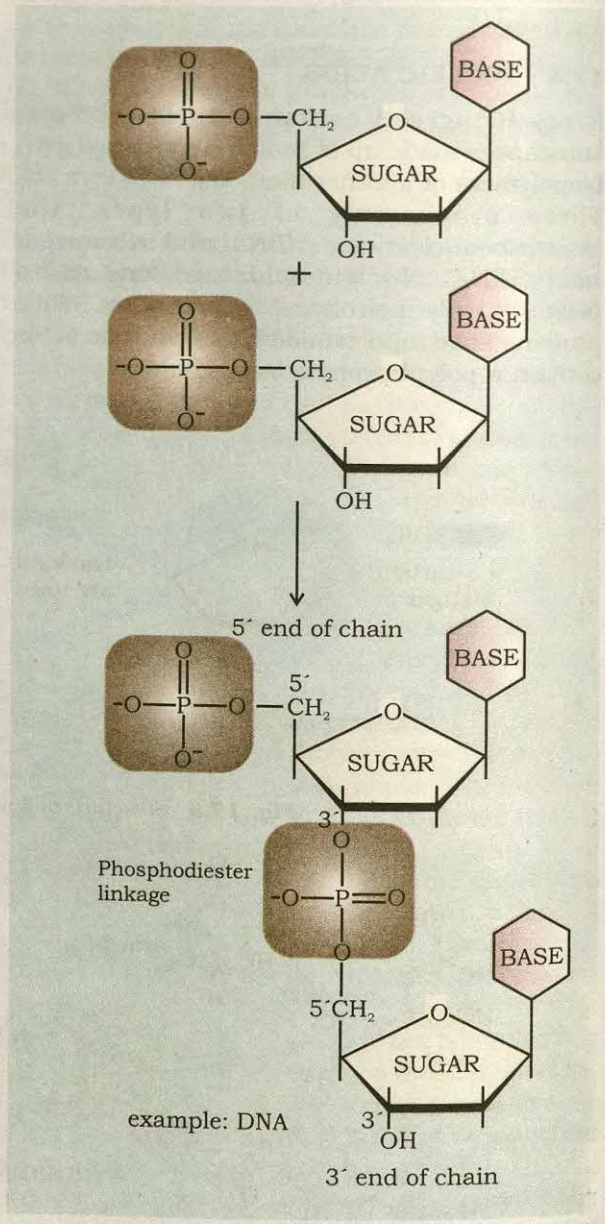


Fig. 17.13 *Formation of a dinucleotide.*

A nucleic acid chain is commonly abbreviated by a one letter code with the 5′end of the chain written at the left e.g., a tetranucleotide having adenine, cytosine, guanine and thymine bases from 5′ end to 3′ end is represented as ACGT.

The backbone is composed of alternating sugar and phosphate bonds. It is extremely time consuming to write the complete structure of these oligonucleotides. In order to simplify, the bases are represented by their respective symbols, the phosphate bond is represented by symbol 'P' and sugar is drawn by simple Fischer projection. Thus, the tetranucleotide ACGT can be drawn as follows;

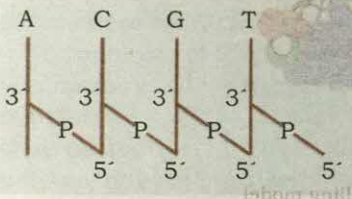


Fig. 17.14 *Tetranucleotide, ACGT.*

17.4.2 DNA – A Double Helix

E. Chargaff found that the base composition in DNA varied from one species to other species, but in all cases the amount of adenine was equal to that of thymine (A = T) and the amounts of cytosine and guanine were also found to be equal (G = C). Therefore, the total amount of purines was equal to the total amount of pyrimidines (A+G= C+T). However, the AT/CG ratio varies considerably between species e.g., this ratio is 1.52 in man while in E. Coli it is 0.93.

In 1953, based on the X-ray diffraction studies of DNA, J. D Watson and F. H. C. Crick proposed a **double helical structure for DNA** which explained not only the base equivalence (A = T; G=C) but also other properties of DNA, specially its duplication in a living cell (*replication*). The double helical structure of DNA is shown in the Fig. 17.15.

The double helix is composed of two right handed helical polynucleotide chains coiled around the same central axis. The two strands are antiparallel, i.e., their (5′→3′) phosphodiester linkages run in opposite directions. The bases are stacked inside the helix in planes perpendicular to the helical axis. It is like a stack of flat plates held together by two ropes of sugar- phosphate polymeric backbone running along outside of stack.

James Dewey Watson

Born in Chicago, Illinois, in 1928, Dr. Watson received his Ph.D. (1950) from Indiana University in Zoology. He is best known for his discovery of the structure of DNA for which he shared with Francis Crick and Maurice Wilkins the 1962 Nobel prize in Physiology and Medicine. They proposed that DNA molecule takes the shape of a double helix, an elegantly simple structure that resembles a gently twisted ladder. The rails of the ladder are made of alternating units of phosphate and the sugar deoxyribose; the rungs are each composed of a pair of purine/ pyrimidine bases. This research laid the foundation for the emerging field of **molecular biology**. The complementary pairing of nucleotide bases explains how identical copies of parental DNA pass on to two daughter cells. This research launched a revolution in biology that led to modern recombinant DNA techniques.

The two strands are held together by hydrogen bonds, shown as black rods in the figure. Only two base pairs i.e. AT and CG fit into this structure. Two hydrogen bonds are formed between A and T (A = T) and three are formed between C and G (C ≡ G). Therefore, CG base pair has more stability as compared to AT base pair (Fig. 17.15). The two complementary base pairs of DNA, i.e., (T-A) and (C-G) with their hydrogen bonds are shown in Fig. 17.16. In addition to hydrogen bonds, other forces e.g. hydrophobic interactions between stacked bases are also responsible for stability and maintenance of double helix.

The diameter of double helix is 2 nm, as shown in Fig. 17.15, the double helical structure repeats at intervals of 3.4 nm (one complete turn), which corresponds to ten base pairs. Two kinds of grooves, one major and one minor are evident in the structure. DNA helices can be right handed as well as left handed. The β-conformation of DNA having the right-handed helices is the most stable. On heating the two strands of DNA separate from each other (known as melting) and on cooling these again hybridize (annealing). The temperature at which the two strands separate completely is known as its melting temperature (T_m) which is specific for each specific sequence. So far we have discussed the secondary structure of DNA. In secondary

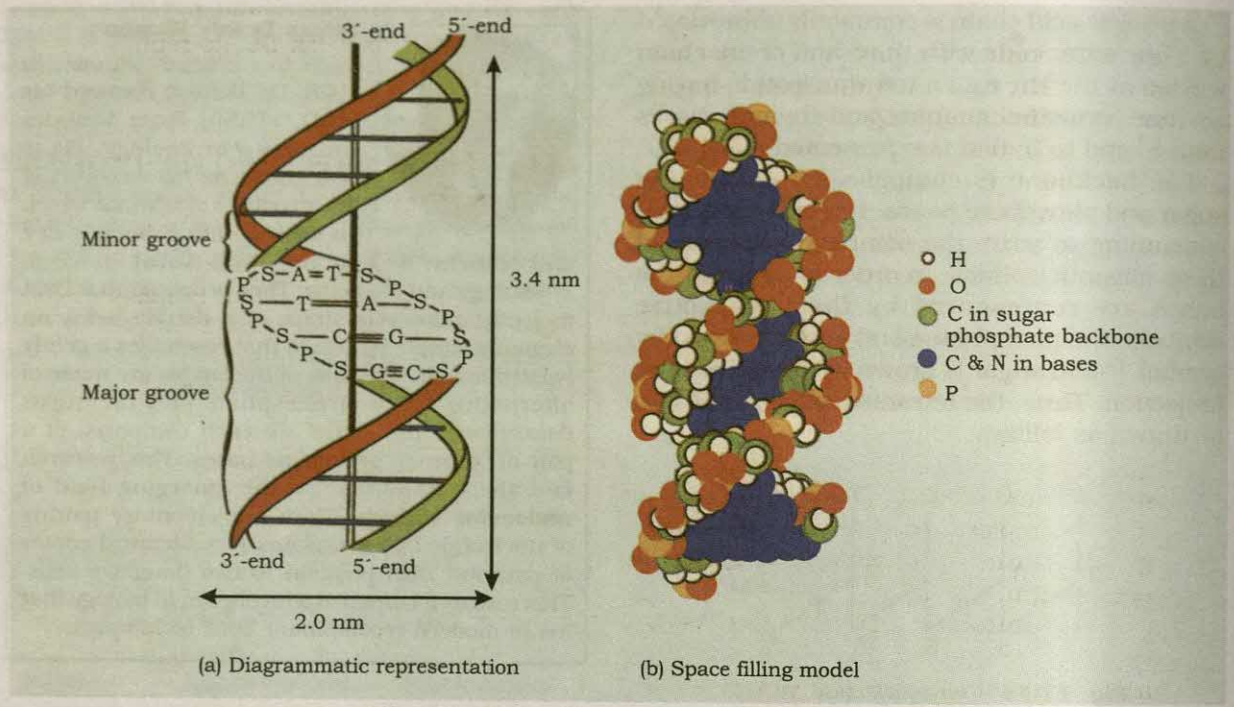


Fig. 17.15 *Double helical structure of DNA.*

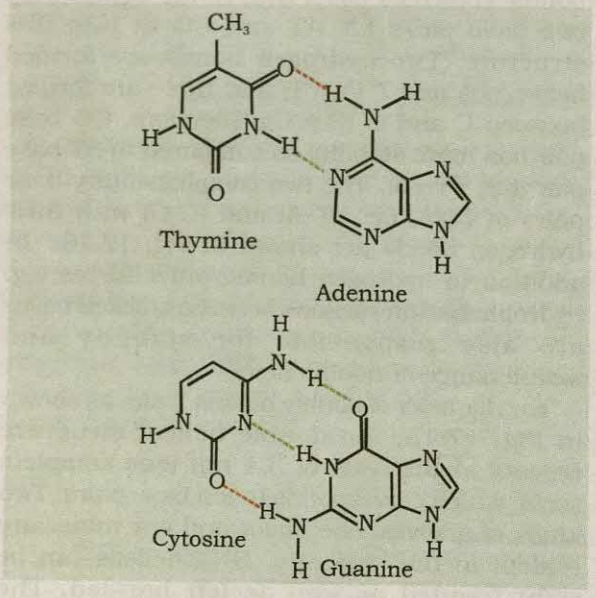


Fig. 17.16 *Hydrogen bonds are formed between complementary base pairs.*

structure of RNA, helices are present but only single stranded. At higher levels one deals with the way these molecules are bound to proteins, folded and supercoiled to make chromatin and chromosomes. Such structures explain how four meters of DNA can be filled inside a single cell.

Example 17.2

The two samples of DNA , A and B have melting temperatures (T_m) 340 and 350 K respectively. Can you draw any conclusion from this data regarding their base content?

Solution

The B sample of DNA having higher T_m must be having more GC content as compared to sample A, since GC base pair having 3 hydrogen bonds as compared to AT base pair having only 2 hydrogen bonds, results in stronger binding.

Example 17.3

In E.coli DNA the AT/GC ratio is 0.93. If the number of moles of adenine in its DNA sample are 465,000, calculate the number of moles of guanine present.

Solution

Since, the number of moles of adenine should be equal to those of thymine, (A+T) = 930,000. Since, A+T/G+C = 0.93, the (G+C)=1000,000. Therefore, the number of moles of guanine should be 1000,000/2 = 500,000.

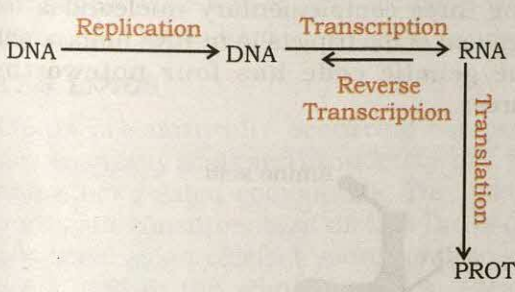
17.4.3 Heredity-the-Genetic Code

Nucleic acids control heredity at molecular level. The double helix of DNA is the store house of the hereditary information of the organism. This information is in the coded form as the sequence of bases along the polynucleotide chain. Since DNA has only four different bases, the genetic message can be compared to a language which has only four letters A, C, G and T.

DNA must preserve this information and also use it in the following manner:

1. DNA molecules can duplicate themselves i.e., can synthesize other DNA molecules identical with the original; this process is known as **replication**.
2. A single strand of DNA can act as a template on which a molecule of RNA is synthesized in a specific manner; this process is known as **transcription**.
3. The RNA molecule in turn directs the synthesis of specific proteins which are characteristic of each kind of organism, this process is called **translation**.

These concepts constitute the central dogma of molecular biology and were summarized by Francis Crick in the following diagram,



In molecular biology, the word transcription is used as a synonym for RNA synthesis and translation as a synonym for protein synthesis. Translation is unidirectional but transcription can sometimes be reversed i.e., RNA is copied into DNA. This reverse transcription occurs during life cycle of some retroviruses.

We can thus infer that base sequence in DNA indirectly controls the sequence of amino acids in the protein. Since protein molecule can contain a maximum of 20 different types of amino acids, it is like a large sentence written in a language of 20 letters, but the hereditary message is written in a language of only 4 letters; it is written in a code with each word of 3 letters (triplet: codon) standing for a particular amino acid. In order to understand fully the genetic code, let us first learn about replication and transcription.

17.4.4 Replication

We have already studied that in the DNA double helix the sequence of bases in one chain is complementary to the sequence in the other chain, therefore one controls the other.

At the time of cell division (mitosis) the two strands of the DNA double helix partly unwind and each serves as a template for the synthesis of a new DNA molecule (Fig.17.17). DNA replication follows the base pairing rules by

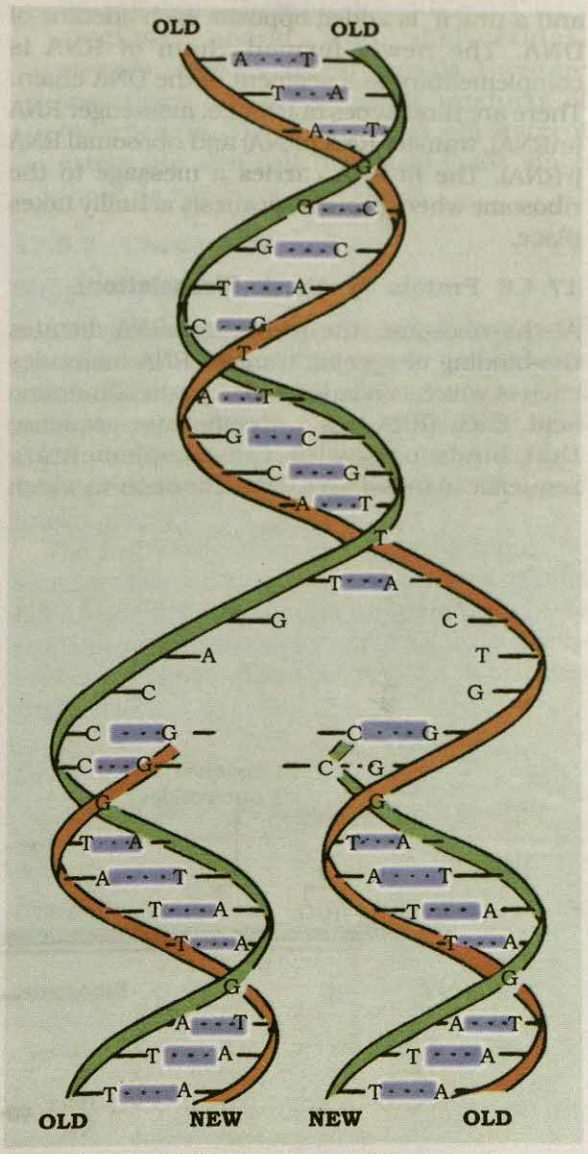


Fig. 17.17 *Machanism of DNA replication.*

which A pairs with T and G pairs with C. Therefore, each daughter molecule is an exact replication of the parent molecule. DNA replication is semi-conservative i.e., only half of the parental DNA is conserved and only one strand is synthesized. DNA replication takes place only in the 5′→3′ direction.

17.4.5 Transcription

This process resembles DNA replication. The double helix of DNA partially uncoils and on one of the two strands is formed a chain of RNA. Here, a ribose sugar is incorporated against a deoxyribose moiety of the parent DNA strand and a uracil is added opposite each adenine of DNA. The newly formed chain of RNA is complementary to a segment of the DNA chain. There are three types of RNA i.e. messenger RNA (mRNA), transfer RNA (tRNA) and ribosomal RNA (rRNA). The m-RNA carries a message to the ribosome where protein synthesis actually takes place.

17.4.6 Protein Synthesis (Translation)

At the ribosome, the messenger RNA dictates the binding of specific transfer RNA molecules each of which is bonded with a particular amino acid. Each tRNA has a specific base sequence that binds only with the complementary sequence in messenger RNA. The order in which the t RNA molecules get attached on mRNA i.e., the sequence in which the amino acids are built into the polypeptide chain depends upon the sequence of bases along the mRNA chain.

Since it is the sequence of four different nucleotides that is used to convey information for the combination of twenty different amino acids into peptide chains, each amino acid must be represented by combination of at least three nucleotides (triplet). This is true since there are only sixteen different doublets of four nucleotides (4^2) but there are 64 triplets (4^3). These 64 three letter code words are known as Codons. However, there being only 20 amino acids, more than one codon can code for the same amino acid e.g., CUU and CUC both can call leucine. Proline is encoded by CCU, CCA, CCG and CCC. Therefore, codons can be synonyms and genetic code is degenerate. A difference of a single base in the DNA molecule or a single error in the reading of the code can cause a change in the amino acid sequence which leads to **mutation**. A diagramatic representation of the mechanism of protein synthesis in given in Fig. 17.18.

It may be noted that every t-RNA molecule has an amino acid attachment site and a site having three complementary nucleotides for recognition of the triplets in m-RNA (*anticodon*).

The genetic code has four noteworthy features;

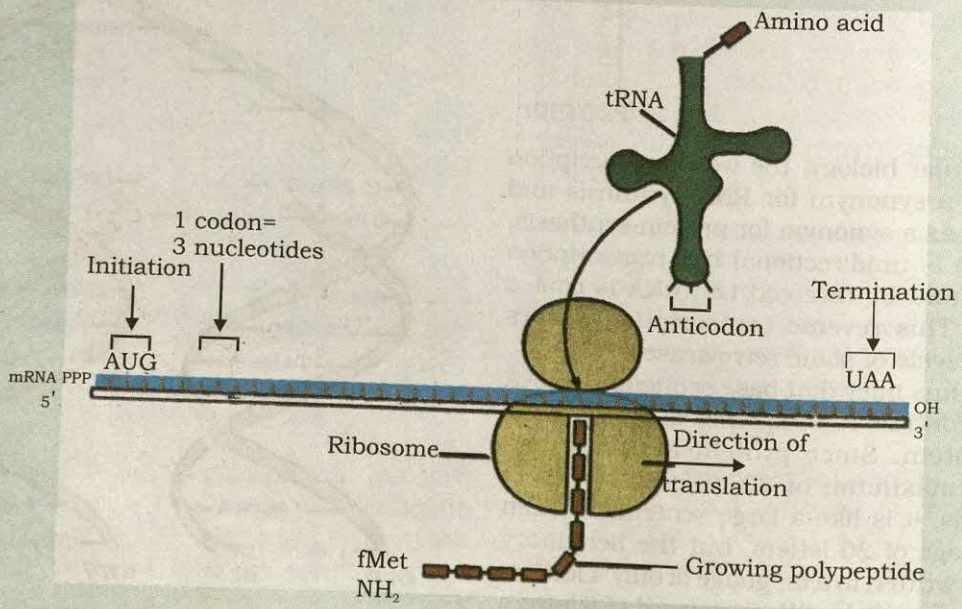


Fig. 17.18 *Diagrammatic representation of protein synthesis.*

Har Gobind Khorana

Har Gobind Khorana, was born in 1922. He obtained his M.Sc. degree from Punjab University in Lahore. He worked with Professor Vladimir Prelog, who molded Khorana's thought and philosophy towards science, work and effort. After a brief stay in India in 1949, Khorana went back to England and worked with Professor G.W. Kenner and Professor A.R.Todd. It was at Cambridge, U.K. that he got interested in both proteins and nucleic acids. Dr Khorana shared the Nobel Prize for Medicine and Physiology in 1968 with Marshall Nirenberg and Robert Holley for cracking the genetic code.

1. It is universal
2. It is degenerate i.e. more than one codons code for an amino acid.
3. It is commaless
4. The third base of the codon is less specific

There is a single code for all living organisms. This is a strong indication that life started on earth about 3 billion years ago and only once the genetic code was established has remained unchanged since then.

17.5 LIPIDS

Lipids are naturally occurring compounds related to fatty acids and include fats, oils, waxes and other related compounds. The lipids are important constituents of diet. In the body the fats serve as an efficient source of energy, and are stored in the adipose tissues. These are hydrophobic in nature and dissolve in organic solvents. *Phospholipids* (lipids containing phosphorous) are important constituents of cell membrane.

17.5.1 Classification

Based on their chemical composition, lipids are classified as follows;

(A) Simple lipids (homolipids): Simple lipids are alcohol esters of fatty acids which include,

1. **Neutral fats (glycerides)**: Also known as triglycerides, these are triesters of fatty acids and glycerol.
2. **Waxes**: These are esters of fatty acids with long chain monohydroxy alcohols. These have higher melting points than neutral fats.

(B) Compound lipids (heterolipids): Lipids with additional groups are called compound lipids. These include:

1. **Phospholipids (phosphatides)**:These contain additional groups e.g., a phosphoric acid, nitrogen containing bases and other substituents.
2. **Glycolipids**: These are esters of fatty acids with carbohydrates, and may contain nitrogen but no phosphorus.

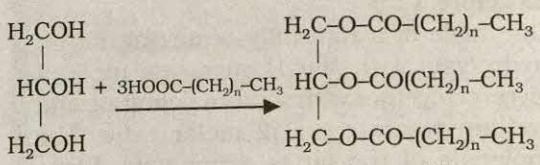
(C) Derived lipids: These are the substances derived from simple and compound lipids by hydrolysis. These include fatty acids, fatty alcohols, mono and diglycerides, steroids, terpenes and carotenoids. These are sometimes present as waste products of metabolism. Glycerides and cholesterol esters are also called neutral lipids since these do not carry any charge.

17.5.2 Chemical Structure

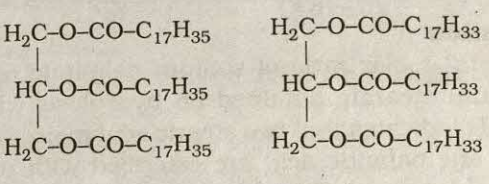
Simple lipids:

1. Glycerides: The triglycerides are esters of glycerol with long chain fatty acids. Fatty acids always have an even number of carbons and may be saturated, e.g. palmitic acid ($C_{15}H_{31}COOH$) and stearic acid ($C_{17}H_{35}COOH$) or unsaturated e.g. oleic acid ($C_{17}H_{33}COOH$) and linolenic acid ($C_{17}H_{29}COOH$).

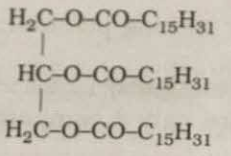
The three fatty acids in triglycerides may be same or different. Fats are glycerides of saturated fatty acids e.g., tripalmitin and tristearin. Oils contain unsaturated fatty acids e.g., triolein. α-Oleo-β-palmito-α´-stearin is an example of mixed triglyceride.



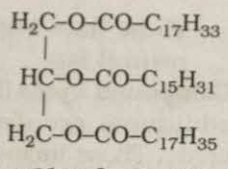
Glycerol **Fatty acid** **Triglyceride (Neutral fat)**



Tristearin **Triolein**



Tripalmitin



α-Oleo-β-palmito-α´-stearin

The presence of double bonds with less stable 'cis' stereochemistry in unsaturated fatty acids e.g. at C-9 in oleic acid ($C_{17}H_{33}COOH$), at C-9 and C-12 in linoleic acid ($C_{17}H_{31}COOH$), at C-9, C-12 and C-15 in linolenic acid ($C_{17}H_{29}COOH$) is of vital biological significance. In solid state, the molecules of saturated fatty acids fit closely together due to their zig-zag tetrahedral structure. The cis unsaturated acid chains have a bend at the double bond and do not fit closely resulting in the lowering of the melting point of the fat.

Example 17.4

An unsaturated fatty acid on ozonolysis yields an aldehyde $H_3C(CH_2)_7CHO$ and an aldehydic monocarboxylic acid $OHC\ (CH_2)_7\ COOH$. Write down the structure and name of the acid.

Solution

An aldehyde function results as a result of ozonolysis of a double bond. Moreover, the doubly bonded carbon atom must carry a hydrogen. Since two aldehydes are formed, the double bond must be –HC=CH-. Therefore, the structure of the unsaturated acid can be written as,

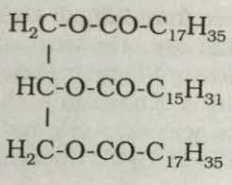
$H_3C(CH_2)_7HC{=}CH\ (CH_2)_7COOH$. It is oleic acid.

Example 17.5

One mole of a naturally occurring fat on hydrolysis with NaOH gave one mole of glycerol together with sodium palmitate and sodium stearate in 1:2 molar ratio. The molecule of the fat is symmetric. Write down the structure of the fat.

Solution

The 1:2 molar ratio of sodium palmitate and sodium stearate obtained on hydrolysis with NaOH indicates that two stearic acid molecules and one palmitic acid are esterified with one mole of glycerol. Since the molecule of fat has symmetry, the two stearic acid molecules must be linked to two terminal primary alcoholic groups. Therefore, the structure of the fat must be;



2. Waxes: These are esters of long chain saturated and unsaturated fatty acids with long chain monohydroxy alcohols. The fatty acids range between C_{14} and C_{36} and the alcohols range from C_{16} to C_{36}. Most of the waxes are mixtures.

17.5.3 Biological Functions and other Applications of Lipids

Fats are important food reserves of animals and plant cells. We can extract animal and vegetable fats and oils from natural sources. While we synthesize fat in our own bodies, we also consume fats synthesized by plants and other animals.

Phospholipids are indispensable structural components of cell membranes and are also used as detergents to emulsify fat for transport within the body. These are never stored in large amounts. Cholesterol is the principal sterol of higher animals, abundant in nerve tissues and gallstones. Cholesterol is not present in plant fats.

17.6 HORMONES

Hormones are molecules that transfer information from one group of cells to distant tissue or organ. These substances are produced in small amounts by various endocrine (ductless) glands in the body. Hormones are delivered directly to the blood stream in minute quantities and are carried by blood to various target organs where these exert physiological effect and control metabolic activities. Therefore, frequently their site of action is away from their origin. Hormones are required in trace amounts and are highly specific in their functions. The deficiency of any hormone leads to a particular disease, which can be cured by the administration of that hormone.

17.6.1 Classification and Functions of Hormones

Hormones may be classified on the basis of (i) their structure or (ii) their site of activity in the cell. Classification based on structure is given in Fig. 17.19.

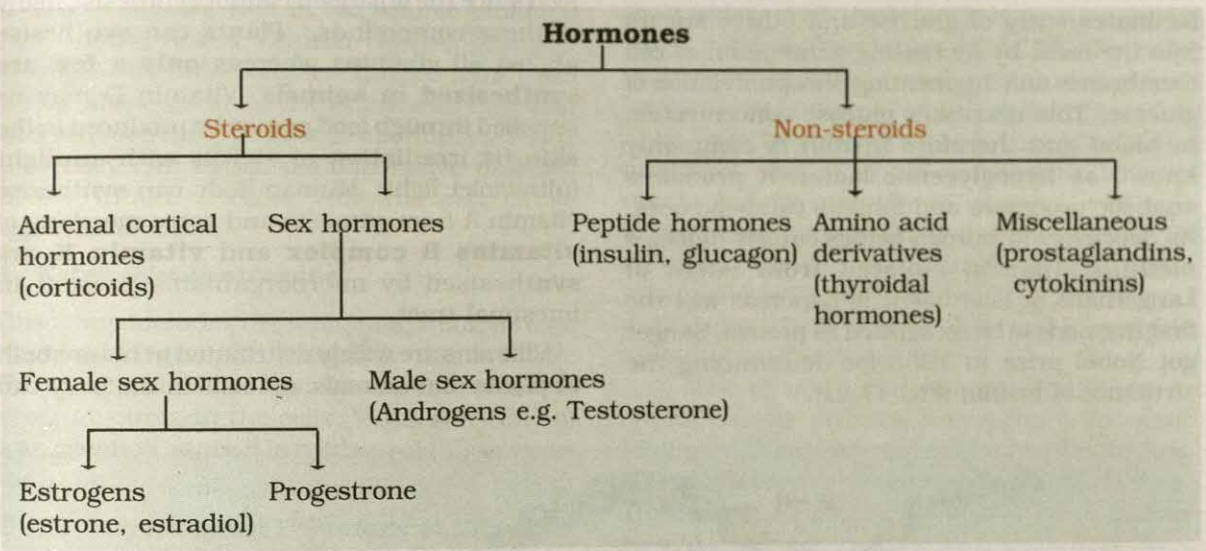


Fig 17.19 *Classification of Hormones*

Steroids on which the above classification is made are compounds whose structure is based on four-ring network, consisting of 3 cyclohexane rings and 1 cyclopentane ring.

The steroid nucleus is found in some vitamins, drugs and bile acids also. The steroids nucleus and a few sex hormones are given in Fig. 17.20.

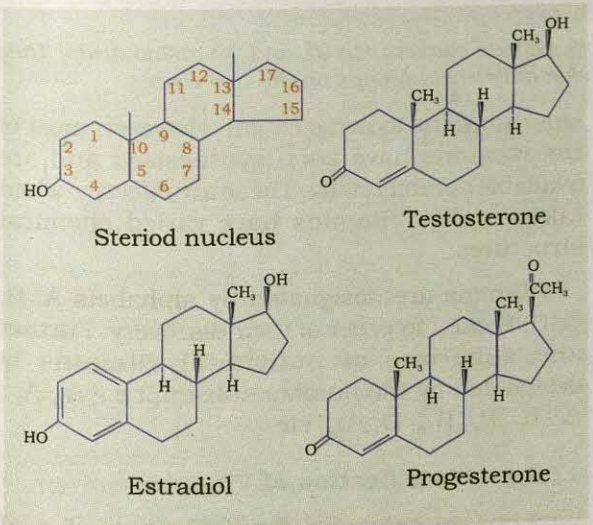


Fig. 17.20 *Structure of few sex hormones*

I. Functions of steroid hormones:

1. Sex hormones: Sex hormones are divided into three groups (i) the male sex hormones, or *androgens*; (ii) the female sex hormones, or estrogens; and (iii) pregnancy hormones, or *progestines*. *Testosterone* is the major male sex hormone produced by testes. It is responsible for male characteristics (deep voice, facial hair, general physical constitution) during puberty. Synthetic testosterone analogs are used in medicine to promote muscle and tissue growth, for example, in pateints with muscular atrophy. Unfortunately, such steroids are also abused and consumed illegally, most commonly by body builders and athletes, even though health risks are numerous. *Estradiol* is the main female sex hormone. It is responsible for development of secondary female characteristics and participates in the control of the menstrual cycle. *Progesterone* is responsible for preparing the uterus for implantation of the fertilized egg. Many steroid hormones, for example, progesterone itself, have played important role as *birth control agents*.

2. Corticosteroids (Adrenal cortical hormones):

(a) *Mineralo corticoids*, made by different cells in the adrenal cortex are concerned with water-salt balance in the body. These regulate NaCl content of blood and cause excretion of potassium in urine.

(b) *Glucocorticoids*, made by adrenal cortex, modify certain metabolic reactions and have an anti-inflammatory effect.

II. Functions of non-steroid hormones:

1. Peptide hormones : Insulin has a profound influence on carbohydrate metabolism. It facilitates entry of glucose and others sugars into the cells, by increasing penetration of cell membranes and augmenting phosphorylation of glucose. This decreases glucose concentration in blood and therefore insulin is commonly known as hypoglycemic factor. It promotes anabolic processes and inhibits catabolic ones. Its deficiency in human beings causes *diabetes mellitus*. Insulin isolated from islets of Langerhans or islet tissue of pancreas was the first hormone to be recognized as protein. Sanger got Nobel prize in 1958 for determining the structure of insulin (Fig. 17.21).

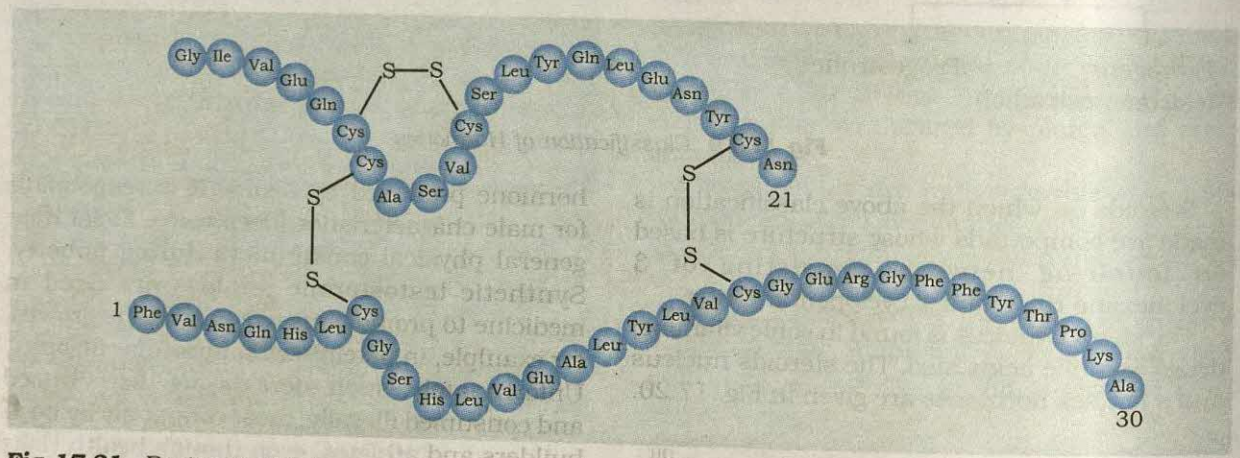


Fig 17.21 *Bovine insulin hormone structure has two polypeptide chains with 21 and 30 amino acids. They are joined by sulfur bridges connecting cysteine amino-acid groups on the two chains.*

2. Amino acid derivatives: The thyroidal hormones e.g. thyroxin and triiodothyronine affect the general metabolism, regardless of the nature of their specific activity. It is for this reason why thyroid gland is known as pace setter of the endocrine system.

Based on the site of activity in the cell, hormones may be divided into two categories. Hormones in the first category affect the properties of the plasma membranes. These include all peptide hormones e.g., insulin and hormones of pituitary gland. In the other category, hormones are taken into the cell and transported to the nucleus where they influence the nature and rate of gene expression.

17.7 VITAMINS

Vitamins can be defined as essential dietary factors required by an organism in minute quantities and their absence causes specific *deficiency diseases*. Vitamins are essential for life and a steady supply of these is required in food since the organism cannot synthesise many of these compounds. Plants can synthesise almost all vitamins whereas **only a few are synthesized in animals**. Vitamin D may be supplied through food or may be produced in the skin by irradiation of sterols with sunlight (ultraviolet light). Human body can synthesise vitamin A from carotene and some members of **vitamins B complex** and **vitamin K** are synthesised by microorganisms present in intestinal tract.

Vitamins are widely distributed in nature both in plants and animals. All cells in the body can store vitamins to some extent. However, most of the vitamins have been synthesised and are available commercially. These are effective when taken orally. Vitamins have varied chemical structures.

Vitamins are designated by alphabets A, B, C, D, E, etc., in order of their discovery. Further any subgroup of individual vitamins is designated by the number subscript e.g. A_1, A_2 , B_1, B_2, B_6, B_{12}, D_1, D_2, etc.

17.7.1 Classification of Vitamins

Vitamins are generally classified into two broad types based on their solubility, i.e., fat soluble

and water-soluble. However, these two groups discharge different functions.

A. Fat soluble vitamins

These are oily substances not readily soluble in water. The group includes vitamins A, D, E and K. Liver cells are rich in fat soluble vitamins e.g. Vitamin A and Vitamin D. This group of hydrophobic, lipid soluble vitamins as a class are not absorbed in the body unless fat digestion and absorption proceed normally. Their deficiency can cause malabsorptive disease. Excess intake of these vitamins may cause *hypervitaminoses*.

B. Water soluble vitamins

This group includes the remaining vitamins e.g., vitamins of B group (B-Complex), vitamin C, etc. The water soluble vitamins are stored in much lesser amounts in the cells. Vitamin H (Biotin) is an exeption, since it is neither soluble in water nor in fat.

17.2.2 Physiological Functions of Vitamins

Vitamins catalyze biological reactions in very low concentration, therefore the daily requirement of any vitamin for any individual is extremely small. However, the daily dose of any vitamin for any individual is not a fixed quantity and varies according to the size, age and rate of metabolism of the individual. Youngsters need higher quantity of vitamins than elders and their requirement increases when a person performs exercise. The need of growing children and pregnant mothers for vitamins is more. The intestinal organisms may synthesize vitamins in significant amounts and play an important role in regulating the quantity of vitamins available to the organism. Most of the vitamins of B-complex group and vitamin K are some vitamins synthesized by the intestinal organisms. These may be absorbed in variable amounts and utilized.

A lack of one or more vitamins leads to characteristic deficiency symptoms in man. Multiple deficiencies caused by lack of more than one vitamin are more common in human beings. This condition of vitamin deficiency is known as **avitaminosis**. In Table 17.3 some important vitamins have been tabulated along with their sources and deficiency diseases.

Table 17.3

S No.	Name of vitamin	Source	Deficiency disease
1	Vitamin A (bright eye vitamin)	Fish oil particularly shark liver oil, liver of fresh water fish rice polishing, liver, kidney.	Xerophthalmia i.e hardening of cornea of eye
2	Vitamin B_1 (thiamin)	Yeast, milk, green vegetables etc	Beri-beri (a disease of nervous system)
3	Vitamin B_2 (riboflavin)	Yeast, vegetables, milk, egg white liver and kidney	Dark red tongue (glossitis), dermatitis and cheilosis (fissuring at corners of mouth and lips)
4	Vitamin B_6 (pyridoxine)	Cereal, grams, molasses, yeast, egg yolk and meat	Severe dermatitis, convulsions
5	Vitamin H (Biotin)	Yeast, liver, kidney and milk	Dermatitis, loss of hair and paralysis
6	Vitamin B_{12}	Liver of ox, sheep, pig, fish etc.	Pernicious anaemia
7	Vitamin C	Citrus fruits, green vegetables	Scurvy
8	Vitamin E	Wheat germ oil, cotton seed oil and soybean oil	Sterility
9	Vitamin K	Cereals, leafy vegetable	Hemorrhagic conditions
10	Coenzyme Q_{10}	Chloroplasts of green plants and mitochondria of animals	Low order of immunity of body against many diseases

SUMMARY

The **biochemical reactions** like chemical reactions follow the laws of chemistry and physics. The energy obtained during oxidation of food, is coupled to the reaction leading to formation of ATP (adenine triphosphate). Many biomolecules e.g., *carbohydrates, proteins, nucleic acids, lipids, hormones* and *vitamins* play a significant role in nature's energy cycle. Amongst carbohydrates glucose is the most important naturally occurring sugar, which plays a key role in release of energy. Proteins, the biopolymers of amino acids are essential for life. As enzymes, these catalyze biochemical reactions, as hormones they regulate metabolic processes and as antibodies these protect the body against toxic substances. All proteins on partial hydrolysis give peptides of varying molecular masses and on complete hydrolysis yield amino acids. The protein structure is studied at different levels, the sequence of amino acids in polypeptide chains present in proteins constitutes it's primary structure. The study of the shape in which the polypeptide chains exist refers to its secondary structure. The complete 3-D form (conformation) of polypeptide chains along with other non-ordered segments is the tertiary/quaternary structure of proteins. *Enzymes* are proteins which are highly specific in biocatalysis.

Nucleic acids, DNA and **RNA** are polymers of nucleotides. DNA has double helical structure while RNA is single stranded. *DNA stores the genetic information in the form of the sequence of bases.* The process in which duplication of DNA takes place during cell division is known as *replication.* During replication the genetic message is passed on to the daughter nuclei. One strand of DNA acts as a template on which a complementary strand of RNA is synthesized. This process is called *transcription.* The newly formed RNA dictates the synthesis of protein at the ribosome. This process is known as *translation.* The sequence of three nucleotides on a polynucleotide chain is known as **codon**. There are 64 codons, each specific for one amino acid.

Lipids are fatty acid derivatives e.g., fats, oils, waxes etc., which are important constituents of diet. Fats are stored in adipose tissue of body as food reserve for spare energy. Phospholipids and lipoproteins are important constituents of cell membrane. **Hormones** are biomolecules produced by endocrine (ductless) glands of the body. These transfer information from one group of cells to a distant organ or tissue and thus control the metabolism. **Vitamins** are essential components of diet. Their deficiency causes specific diseases.

EXERCISES

17.1 What are the two stages of photosynthesis in a green plant? Give the basic equation of photosynthesis.

17.2 What are reducing and non-reducing sugars? What is the structural feature characterizing reducing sugars?

17.3 Draw open chain structure of aldopentose and aldohexose. How many asymmetric carbons are present in each?

17.4 Draw simple Fischer projections of D- and L-glucose. Are these enantiomers?

17.5 Draw Fisher projections of L- galactose and L- mannose.

17.6 Write down the structures and names of the products obtained when D-glucose is treated with (i) acetic anhydride (ii) hydrocyanic acid (iii) bromine (iv) conc.HNO_3 and (v) HI

17.7 Enumerate the reactions of glucose which can not be explained by its open chain structure.

17.8 Explain mutarotation. Give its mechanism in case of D-glucose.

17.9 Amylose and cellulose are both straight chain polysaccharides containing only D-glucose units. What is the structural difference between the two?

17.10 What are essential and nonessential amino acids? Give two examples of each. Give reasons for the following.

(i) Amino acids have relatively higher melting point as compared to corresponding halo acids

(ii) Amino acids are amphoteric in behaviour

(iii) On electrolysis in acidic solution amino acids migrate towards cathode while in alkaline solution these migrate towards anode.

(iv) the monoamino monocarboxylic acids have two pK values

17.12 If three amino acids viz., glycine, alanine and phenylalanine react together, how many possible tripeptides can be formed? Write down the structures and names of each one. Also write their names using three and one letter abbreviations for each amino acid.

17.13 What type of linkages are responsible for the formation of,

(i) Primary structure of proteins

(ii) Cross linking of polypeptide chains

(iii) α- Helix formation

(iv) β- Sheet structure

17.14 Which forces are responsible for the stability of α-helix? Why is it named as 3.6_{13} helix?

17.15 What is denaturation and renaturation of proteins?

17.16 Define enzymes. How do enzymes differ from ordinary chemical catalysts? Comment on the specificity of enzyme action. What is the most important reason for their specificity?

17.17 What are the products obtained on complete hydrolysis of DNA? Write down the structure of pyrimidine and purine bases present in DNA.

17.18 Enumerate the structural differences between DNA and RNA. Write down the structure of a nucleoside, which is present only in RNA.

17.19 What are complementary bases? Draw structure to show hydrogen bonding between adenine and thymine and between guanine and cytosine.

17.20 What is the melting temperature (*Tm*) of DNA? A DNA molecule with more number of GC base pairs than AT base pairs has higher *Tm* than the one with lesser number of GC base pairs than AT base pairs. Explain why?

17.21 When RNA is hydrolyzed there is no relationship among the quantities of four bases obtained unlike DNA. What does this fact indicate about the structure of RNA?

17.22 How does DNA replicate? Give the mechanism of replication. How is the process responsible for preservation of heredity?

17.23 Genetic code is degenerate. Comment.

17.24 Answer the following about protein synthesis,

(i) Name the location where protein synthesis occurs.

(ii) How do 64 codons code for only 20 amino acids?

(iii) During translation which one of the two-end functional groups of the polypeptide is formed first?

(iv) Which of the two bases of the codon are most important for coding, the first two or last two?

17.25 How are lipids classified? Give an example of each class.

17.26 An unsaturated fatty acid having formula $C_{17}H_{33}COOH$ has a double bond at C-9. Amongst two stereoisomers of the acids i.e. cis and trans, which do you expect to have higher m.p.? Explain why?

17.27 'Hormones are chemical messengers'. Explain.

17.28 Comment briefly on the chemical nature of insulin and its physiological activity.

17.29 Define and classify vitamins. Give at least two examples of each type.

17.30 Name the deficiency diseases caused due to lack of vitamin A, C, E, B_1, B_{12} B_6, and K.

UNIT 18

CHEMISTRY IN EVERYDAY LIFE

OBJECTIVES

After studying this Unit, you will be able to:

- describe the applications of analgesics, tranquilizers, antiseptics, disinfectants, antibiotics, antihistamines, antifertility drugs and antacids.
- explain the process of dyeing and classify various dyes.
- know the various chemicals used in preparing creams, perfumes, talcum powders and deodorants.
- understand the terms : preservatives, sweetening agents, antioxidants and edible colours.
- explain pheromones, sex attractants and judge the specificity attached in their action.
- classify detergents into anionic, cationic and nonionic categories.
- describe the chemistry of carbon fibres, ceramics and microalloys.
- describe propellant action and list various propellants used to power rocket motors.

"Mankind owes much to chemistry. The main aim of chemistry has been to improve the quality of life."

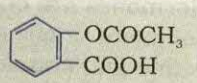
Chemistry plays a major role in all walks of our lives. Our daily needs of food, clothing, shelter, potable water, soaps/detergents (toiletries), medicines, etc., are in one or the other manner connected with chemical compounds. Further, as you must have read by going through the earlier Units, chemistry is the backbone of bulk of industrial materials like glass, cement, fetrilizers, pesticides, paper, polymers, oil, fats, fuels etc., which are so very essential for the sustenance of our lives. Chemistry, infact, is the single branch of science which profoundly influences the existence of human beings and the habitat.

18.1 CHEMICALS IN MEDICINES AND HEALTH CARE

In the ancient practices of treatment of disease like Ayurvedic, the Unani systems or the modern allopathic system, the drugs used are chemical compounds of natural or synthetic origin. Here we discuss some specific classes of drugs used in allopathy.

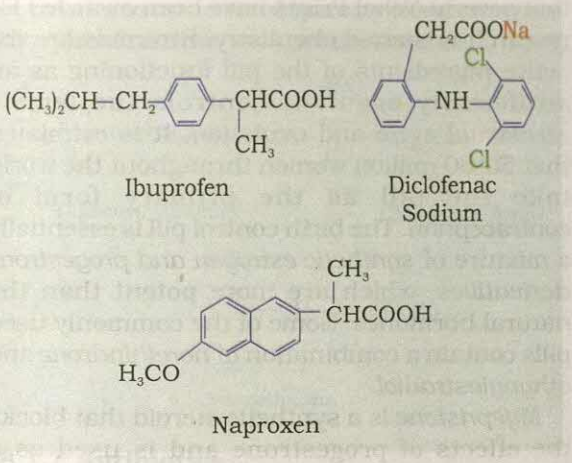
18.1.1 Analgesics

Analgesics are the drugs used for relieving pain. Aspirin (2 – acetoxybenzoic acid) is a common analgesic, with antipyretic (temperature lowering) properties. Aspirin now finds use in the prevention of heart attacks as it has anti-blood clotting action. Many other potential applications of aspirin presently under investigation, include pregnancy-related



Aspirin

complications, viral inflammation in AIDS patients, dementia, Alzheimer's disease and cancer. Despite its popularity, aspirin is supposed to be toxic to the liver. It sometimes causes bleeding from stomach wall and is a gastric irritant. Because of these shortcomings, other analgesics like *naproxen, Ibuprofen* and *diclofenac sodium or potassium* find use as alternatives. Certain narcotics (which induce sleep and unconsciousness) like *morphine* and its derivatives *codeine* and *heroin* are used in severe pain as analgesics.

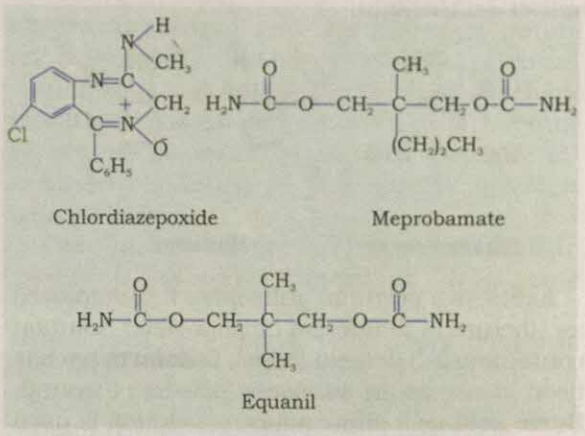


It may be emphasized here that even now aspirin is the drug of choice for the prevention of heart atttacks and as a reliever of pain in angina.

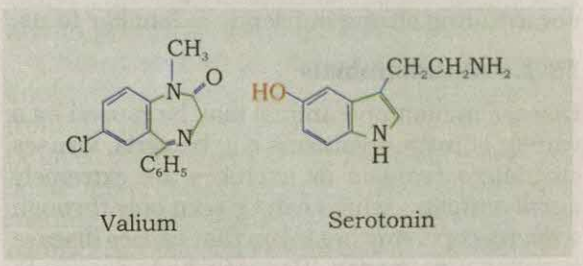
18.1.2 Tranquilizers

Tranquilizers are a class of chemical compounds used for the treatment of stress, mild and severe mental diseases. These are used to relieve stress, fatigue, by inducing a sense of well being. They form an essential component of sleeping pills. Tranquilizers also form an important category of the so called psychotherapeutic drugs. **Derivatives of barbituric acid viz. veronal, amytal, nembutal, luminal and seconal** are familiar drugs of this class. These derivatives are called **barbiturates**. Barbiturates are hypnotic, i.e. sleep producing agents. In addition to the barbiturates, a large number of other nonhypnotic tranquilizers are known. Some important compounds of this class are discussed below:

Chlordiazepoxide and Meprobamate are relatively mild tranquilizers suitable for relieving tension. Equanil is used in controlling depression and hypertension.



Some other substances used as tranquilizers are as follows:

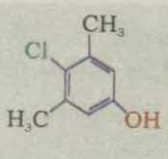


18.1.3 Antiseptics and Disinfectants

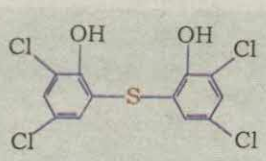
Antiseptic are the chemicals which either kill or prevent the growth of microorganisms. Antiseptics are applied to living tissues. They can be applied to wounds, cuts, ulcers and diseased skin surfaces. All of us must have used antiseptic creams like furacin, soframycin, etc. at one or other time. Disinfectants also kill microorganisms but are not safe for living tissues. These are applied for inanimate objects such as floors, drainage systems, instruments etc. The same substance can act as an antiseptic as well as a disinfectant by varying its concentration. Thus a *0.2 percent solution of phenol is an antiseptic while its 1 percent solution is a disinfectant.*

Chlorine in concentration of 0.2 to 0.4 parts per million (ppm) is used as a disinfectant for drinking water. Low concentrations of **sulphur dioxide** are used for sterilizing and preservation of squashes. Commonly used antiseptic, **dettol** is a mixture of chloroxylenol and terpeneol. **Bithional** is added to soap to impart antiseptic

properties. It eliminates undesirable odours resulting from bacterial decomposition of organic matter on the skin.



Chloroxylenol



Bithional

Iodine is a powerful antiseptic. It is employed as tincture of iodine, an alcohol-water solution containing 2-3 percent iodine. **Iodoform** too has been in use as an antiseptic powder of wound. **Boric acid** as a dilute aqueous solution is used as a weak antiseptic for eyes . It also forms part of antiseptic baby talcum powders.

The use of **hydrogen peroxide** as nonirritating strong antiseptic is familiar to us.

18.1.4 Antimicrobials

Disease in man and animal may be caused by a variety of microorganisms e.g. bacteria, viruses etc. Microorganism or microbes are extremely small oranisms which can be seen only through a microscope. Any organism that causes disease is called a **pathogon**. However, body possesses an efficient natural defence mechanism, which operates at all times against potential pathogenic microbes. In fact skin is impervious to microbes. Many body secretions either kill the microbes or inhibit their growth. Examples are lysozyme (a lipid splitting enzyme) in tears, nasal secretion and saliva, fatty acids and lactic acid in sweat and sebaceous secretions, and hydrochloric acid in stomach. A breach in defence mechanism allows the pathogens to reach tissues, and this causes infection. Invasion and multiplication of a organism in the infected host result in the onset of disease due to the destruction of the normal cell metabolism. In addition, toxins (toxic substances) produced by the microbes may adversely affect the tissues or organs of the host. The control of microbial diseases can be achieved in three ways by:

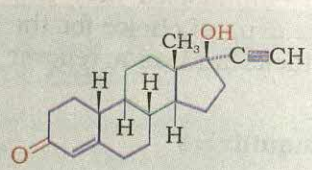
- a drug which kills the organism in the body (bactericidal),
- a drug which inhibits or arrests the growth of the organism (bacteriostatic) and
- increasing immunity and resistance to infection of the body.

Antibiotics are the class of drugs used as antimicrobials. These are discussed in detail in section (18.1.7).

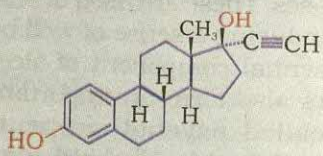
18.1.5 Antifertility Drugs

In highly populated countries, population control has assumed prime importance. One of the most convenient and widely used method of birth control is the use of oral contraceptives. Oral contraceptives belong to the class of natural products known as steroids. The importance of these compounds can be assessed by the fact that several Nobel Prizes have been awarded for research in steroid chemistry. Streroids are the active ingredients of the pill functioning as an antifertility agent. It controls the female menstrual cycle and ovulation. It is estmiated that 50-60 million women throughout the world take the pill as the primary form of contraception. The birth control pill is essentially a mixture of *synthetic estrogen and progestrone derivatives*, which are more potent than the natural hormones. Some of the commonly used pills contain a combination of *norethindrone* and *ethynylestradiol.*

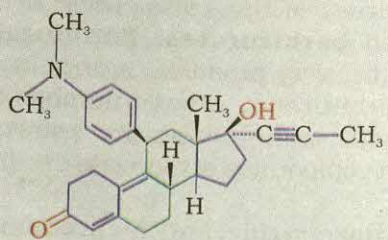
Mifepristone is a synthetic steroid that blocks the effects of progestrone and is used as a "morning after pill" in many countries.



Norethindrone



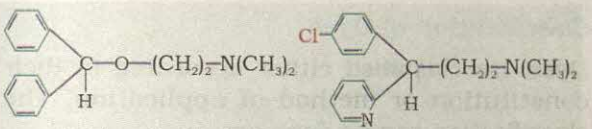
Ethynylestradiol



(Mifepristone)

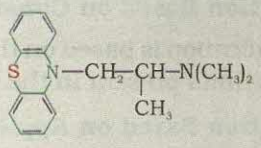
18.1.6 Antihistamines

These drugs are also called as anti-allergic drugs and are used to treat allergy e.g. skin rashes. Since the allergic reactions are caused due to liberation of histamine in the body that is why these drugs are called antihistamines. Other than skin rashes these drugs are useful for conjunctivitis (inflammation of conjunctiva of eye) and rhinitis (inflammation of nasal mucosa). In seasonal rhinitis and conjunctivitis, these drugs relieve sneezing, nasal discharge and itching of eyes, nose and throat. Common drugs of this group are **diphenylhydramine**, **chlorpheniramine** and **promethazine**.



Diphenylhydramine

Chlorpheniramine



Promethazine

18.1.7 Antibiotics

Antibiotics are chemical substances produced by microorganism (bacteria, fungi and mould) that inhibit the growth or even destroy microorganisms. The development of synthetic methods has however, resulted in a modification of this definition. An antibiotic now refers to a substance (produced wholly or partly by chemical synthesis), which in low concentration inhibits the growth or destroys microorganisms by intervening in their metabolic processes. Antibiotic therapy has been likened to 'setting one thief against another'. This is because antibiotics themselves are products of microbial growth. The first antibiotic, discovered by Alexander Fleming in 1929 from the mould Penicillium notatum, was penicillin.

The antibiotics can be either bactericidal or bacteriostatic

Bactericidal	**Bacteriostatic**
Penicillin	Erythromycin
Aminoglycosides	Tetracycline
Ofloxacin	Chloramphenicol

The full range of microorganisms attacked by an antibiotic is called its spectrum. Broad spectrum antibiotics are medicines effective against several different types of harmful microorganisms, e.g. **tetracycline**, **chloramphenicol** and a mixture of potent antibiotics. Penicillin has a narrow spectrum.

Ampicillin and Amoxicillin are semi-synthetic modifications of penicillin. It has become absolutely essential to test the patients for sensitivity (allergy) to penicillin before it is administered.

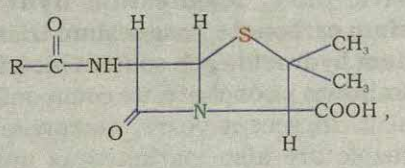
The industrial production of penicillin involves the development of large-scale fermentation techniques. The original microbial strain used by Fleming, Penicillium notatum, was found to give low yields in industry. An alternate strain, Penicillin chrysogenum and its mutant is used in commercial production.

In India, penicillin is manufactured at the Hindustan Antibiotics in Pimpri and at Indian Drugs and Pharmaceuticals Limited, Rishikesh and in private sector of indusry.

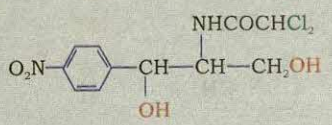
Chloramphenicol is a broad spectrum antibiotic, isolated in 1947. It is rapidly absorbed from the gastro-intestinal tract and hence can be given orally in case of typhoid, dysentery, and acute fever, certain form of urinary infections, meningitis and pneumonia. *Vancomycin* and *ofloxacin* are the other important broad spectrum antibiotics. The antibiotic *dysidazirine* is supposed to be toxic towards certain strains of cancer cells.

Sulpha Drugs

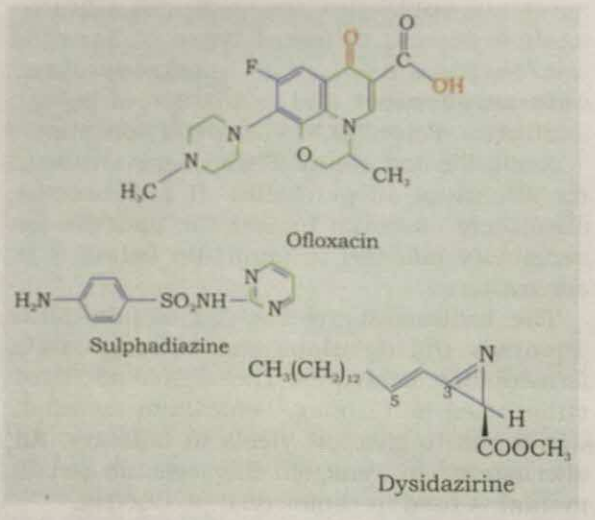
Sulpha drugs like **sulphanilamide**, **sulphadiazine** and **sulphaguanidine** act against microorganisms and have been used as alternatives to antibiotics. These are not in much use at present



General Structure of Pencillin



Chloramphenicol



Ofloxacin

Sulphadiazine

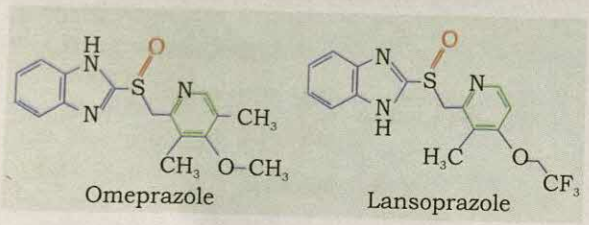
Dysidazirine

Alexander Fleming (1881-1955)

Alexander Fleming after graduating in medicine in 1906 from St. Mary's Medical School, worked with Professor Almorth Wright in bacteriology. He discovered natural bodily secretions, which could combat harmful microbes. Fleming produced a chemical substance, called Penicillin which could destroy certain microbes in the body. Thus, Fleming opened the door to a wonderful natural healer. In 1945, Alexander Fleming, received Nobel Prize for his discovery of Penicillin.

18.1.8 Antacids

Substances which remove the excess acid and raise the pH to appropriate level in stomach are called antacids. Acid Gastritis is one of the commonest ailments associated with digestion. It is caused by excess of hydrochloric acid in the gastric juice. **Magnesium hydroxide, magnesium carbonate, magnesium trisilicate, aluminium hydroxide gel, sodium bicarbonate and aluminium phosphate** are commonlly used as antacid. In recent years, omeprazole and lansoprazole are also marketed as antacids. These prevent formation of acid in the stomach.



Omeprazole Lansoprazole

18.2 DYES

From early times man discovered ways of extracting dyes from natural sources. India has a rich tradition of using natural dyes for making coloured fabrics. Probabaly, the earliest known dyes were indigo (a blue dye) and alizarin (a red dye). These were obtained from plants. Indigo was primarily produced in India and exported all over the world. *A dye is a coloured substance that can be applied in solution or dispersion to a substrate, giving it a coloured appearance.* Usually the substrate is a textile fibre, but it can also be paper, leather, hair, fur, plastic material, wax, a cosmetic base or a foodstuff.

Classification of Dyes

Dyes are classified either according to their constitution or method of application. The classification can be done as:

Classification Based on Constitution

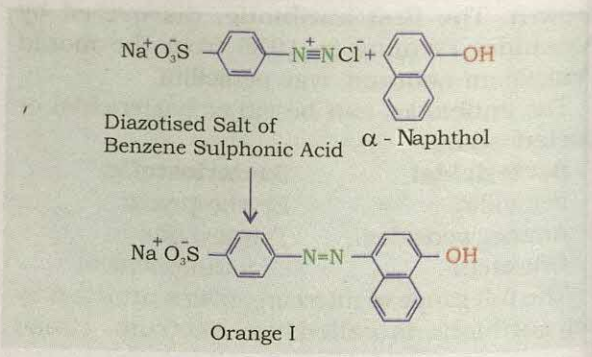
This classification is based on the distinguishing structural units present in the dye (Table 18.1).

Classification Based on Application

Depending upon the process of application the dyes are classified as :

(a) Acid dyes (b) Basic dyes (c)Direct dyes (d) Disperse dyes (e) Fibre reactive dyes (f) Insoluble azo dyes (g) Vat dyes (h) Mordant dyes

(a) Acid dyes: These dyes are usually salts of sulphonic acids and can be applied to wool, silk, polyurethane fibres and nylon. The affinity of acid dyes for nylon is higher than that for other types because polycaprolactum fibres contain a higher proportion of free amino groups. Acid dyes do not have affinity for cotton. *Orange I*, a versatile acid dye is prepared by coupling diazotised sodium salt of benzene sulphonic acid with α - naphthol.

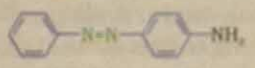
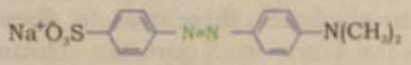
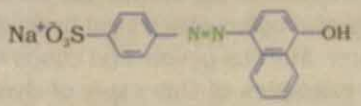
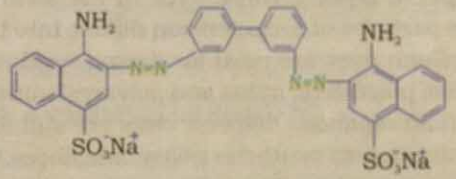
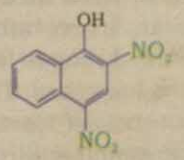
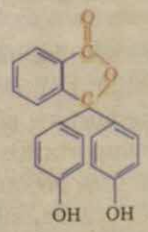
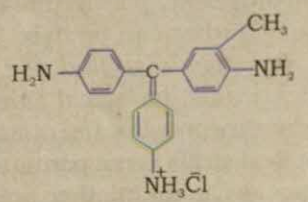
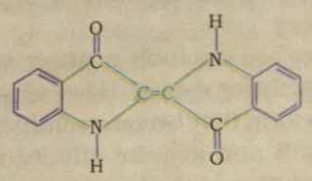
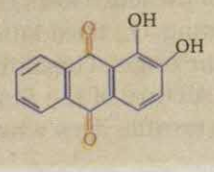


Diazotised Salt of Benzene Sulphonic Acid

α - Naphthol

Orange I

Table18.1 Classification of some Important Dyes Based on constitution.

Name of the Dye	Class of the Dye	Structural Formula
Aniline yellow	Azo	
Methyl Orange	Azo	
Orange I	Azo	
Congo red	Azo	
Martius yellow	Nitro	
Phenolphthalein	Phthalein	
Magenta	Triphenyl Methane	
Indigo	Indigoid	
Alizarin	Anthraquinone	

b) Basic Dyes: Basic dyes contain amino groups which in acid form water soluble salts. These dyes get attached to the anionic sites present on the fabrics. Such dyes are used to dye reinforced nylons and polyesters. *Aniline yellow* and *malachite green* belong to this class of dyes.

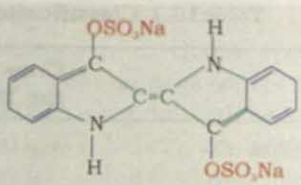
c) Direct Dyes : These are water soluble dyes. As the name suggestes, these dyes are directly applied to the fabric from aqueous solutions and are practically suited for fabrics like cotton, rayon, wool, silk and nylon which form hydrogen bonds with water. *Martius yellow* and *congo red* are important examples of this class of dyes.

d) Disperse Dyes : These dyes in the form of minute particles of a suspension diffuse into the fabric. Such dyes are used for dyeing synthetic fibres like polyesters, nylon and polyacrylonitrile. Many *anthraquinone* disperse dyes are suitable for application to synthetic polyamide fibres.

e) Fibre reactive dyes: These dyes attach themselves to the fibre by an irreversible chemical reaction. Obviously, the dyeing is fast and the colour is retained for a long time. The bonding is through the substitution of leaving group of dye via the hydroxy or amino group of fibres (cotton, wool or silk).

f) Insoluble azo dyes : These dyes are obtained by coupling phenols, naphthols, arylamines, aminonaphthols adsorbed on the surface of a fabric with a diazonium salt. The importance of azo dyes is shown by the fact that they account for over 60% of the dyes used. Cellulose, silk, polyester, nylon, polypropylene, polyurethanes, polyacrylonitriles and leather can be dyed by using these dyes. *Azo dyes also find use in foodstuffs, cosmetics, drugs, biological stains and as indicators in chemical anaylsis.* Use of such dyes for colouring of food stuffs is not permitted now. Their use is now declining in other areas also.

g) Vat dyes: Vat dyes are insoluble in water and cannot be used directly for dyeing. However, on reduction to a leuco form they become soluble in presence of an alkali and acquire affinity for cellulose fibres. A solution of the leuco form can be applied for dyeing or printing. On reoxidation (usually in presence of air) the original insoluble dye is formed within the structure of the fibre. *Indigo* and *Indigosol O* are versatile dyes which belong to this class.



Indigosol O

Indigosol O is readily soluble in water, has affinity for cellulose and can be rapidly and quantitatively oxidized on the fibre with formation of indigo. It is especially suitable for wool.

h) Mordant dyes : These dyes are primarily used for dyeing of wool in the presence of metal ions. The metal ion binds to the fabric and the dye acting as ligand coordinates to the metal ion. The same dye in the presence of different metal ions imparts different colours to the fabrics. Alizarin imparts rose red, blue, brownish red, violet and red colour to the fabric in the presence of Al^{3+}, Ba^{2+}, Cr^{3+}, Mg^{2+}, and Sr^{2+}, ions respectively.

18.3 COSMETICS

The word cosmetics is derived from the Greek word *Kosmetikos*. It means decorating, beautifying or improving complexion of skin. In India from the ancient times *Henna* has been used to decorate hands and some other parts of the body. Some of the cosmetics which find use in daily life are discussed below.

18.3.1 Creams

Creams are used for facial make-up. These are often classifed as: cleansing creams, cold creams, vanishing creams, sunburn creams and bleach creams.

Cleansing Creams: remove facial make up, surface grime, lipstic and oil.

Cold Creams: lubricate the skin and prevent roughness and chaffing.

Vanishing Creams: keep the skin cool and oily.

Sunburn Creams: save the skin from sunburn in summer.

Bleach Cream: exert a bleaching effect on dark skin.

18.3.2 Perfumes

Perfumes are the materials, used to provide fragrance. Several requirements have to be fulfilled to make a good perfume and any material, which just gives good smell, may not be a perfume.

A perfume invariably consists of three ingredients: a vehicle, fixative and odour producing substance.

Vehicle

The vehicle is also called solvent. The role of the solvent is to keep the odour-producing substances in solution. Ethanol and water mixture is the most common vehicle used in perfumery.

Fixative

The function of the fixative is to equalize the rate of evaporation of various odouriferous components of the perfume by suitably adjusting their volatility. *Sandalwood oil* finds use as fixative. Other substances used as fixative are *benzoin, glyceryl diacetate* and esters of cinnamyl alcohol.

Odourous Substances

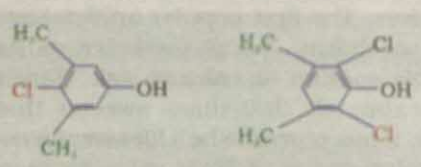
Both natural and synthetic substances are used to impart odour to a perfume. For example, terpenoids like linalool which occur in essential oils are natural odour producing compounds, while anisaldelyde (*p*-methoxybenzaldehyde), is a synthetic odour producing compound.

18.3.3 Talcum Powder

Talcum powder is used to reduce irritation of the skin. Talcum powders like face powders contain talc ($Mg_3(OH)_2Si_4O_{10}$). Chalk, zinc oxide, zinc sterate and a suitable perfume act as the other main constituents of talcum powder. Often specific ingredients like antiseptic and cooling agents are added. The role of the talc is to act as a powder base and to make skin smooth. Chalk absorbs secretion (perspiration) without showing any evidence of such absorption. Zinc oxide masks enlarged pores and minor blemishes, whereas zinc sterate makes powder adhere to skin. Baby talcum powders contain considerable amounts of zinc stearate for adhesiveness and boric acid, for antiseptic purposes. Talcum powders need to be dusted with care to prevent inhalation of the fine particles, which irritate the lungs.

18.3.4 Deodorants

As the name suggests, deodorants are applied primarly to mask the body odour. The body odour results from the bacterial action following perspiration. A deodorant must therefore, possess anti-bacterial properties. Aluminium salts, have been found to possess excellent antibacterial properties. In addition to aluminium salts, ZnO, ZnO_2 and $(C_{17}H_{35}COO)_2Zn$ also find use in deodorant preparations because they are astringents as well as antiseptics. Phenolic antibacterials, which have figured as effective body deodorant are parachlorometaxylenol and dichlorometaxylenol having following structures.



p - Chlorometaxylenol Dichlorometaxylenol

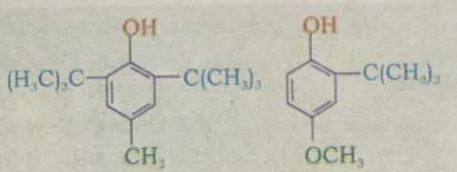
Powder formulations generally have deodorants.

18.4 CHEMICALS IN FOOD

Many chemicals are added to food for their preservation and enhancing their appeal. These include flavourings, sweeteners, dyes, antioxidants, fortifiers, emulsifiers and antifoaming agents. With the exception of the preservatives, fortifying agents, antioxidants and artificial sweeteners, the remaining classes of chemicals mentioned above are added either for ease in processing or for cosmetic purposes, in the real sense these have no nutritive value.

18.4.1 Antioxidants

Antioxidants are the important and necessary food additives. These compounds retard the action of oxygen on the food and thereby help in its preservation. These act as sacrificial materials, i.e., these are more reactive towards oxygen than are the materials they are protecting. They also reduce the rate of involvement of free radicals in the aging process. The two most familiar antioxidants used are *butylated hydroxy toluene (BHT)* and *butylated hydroxy anisole (BHA)*. The additon of BHA to butter increases its storage life from months to years. The two have the following structures.



(BHT) (BHA)

Sometimes BHT and BHA are added in combination with citric or ascorbic acids to produce a more active synergietic effect. Sulphur dioxide and sulphite are useful antioxidants for wine and beers, sugars syrups and cut peeled or dried fruits and vegetables.

18.4.2 Artificial Sweeteners

The artificial sweeteners are another type of food additives. The first popular artificial sweetener was saccharin. It was marketed as its water soluble sodium or calcium salt. Saccharin is approximately 300 times sweeter than cane sugar. It has proved to be a lifesaver for countless diabetics and is of great value to people who need to control intake of calories.

Besides saccharin, the other commonly marketed artificial sweeteners are described here.

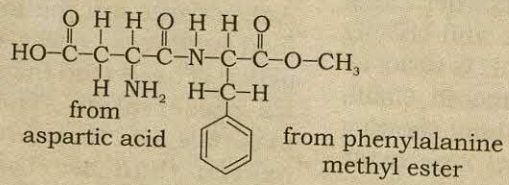
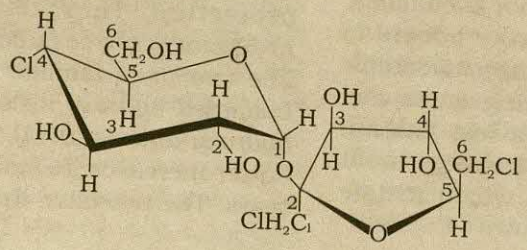
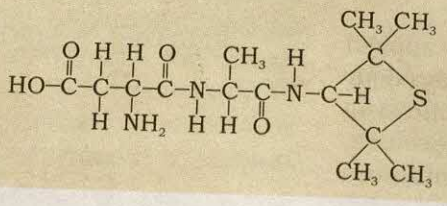
Aspartame is unstable at cooking temperatures, limiting its use as a sugar substitute to cold foods and soft drinks. Alitame is more stable than aspartame during cooking. One potential problem with alitame and similar type of high-potency sweetners is the difficulty in controlling sweetness of food. Sucralose is predicted to become a great commercial success.

18.4.3 Preservatives

Platability and wholesomeness of many food reaches a peak at harvest-time. Often food is most appetizing when it comes from the production line in the food processing plant. However, during storage and distribution undesirable changes occur in flavour, colour, texture and appetitic appeal. The food producers use various preservative to delay these changes. The preservatives prevent spoilage of food due to microbial growth. The most common preservative used is sodium benzoate, C_6H_5COONa. It is metabolized by conversion to hippuric acid, $C_6H_5CONHCH_2COOH$ which ultimately is excreted in the urine. Salts of propionic acid and sorbic acid are also used as preservatives.

18.4.4 Edible Colours

Edible colours used for food are essentially dyes. The use of food dyes is extremely wide spread. They are used to colour everything from meat to fruit. For example, dyes are used to dye orange

Artificial Sweetner	Structural Formula	Sweetness value in comparison to cane sugar
Aspartame		160
Sucralose		650
Alitame		2000

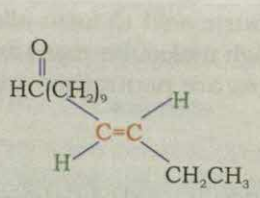
peels so that oranges retain their colour. Colour is one of the ingredients in fruit juices. There is a great deal of controversy over the potential harm the dyes may cause. This controversy becomes more meaningful particularly keeping in view the fact that food dyes add nothing to the nutritive value of food. The use of azo dyes has raised considerable anxiety in that some of them are dangerous for young children and asthma patients. Tetrazine, a very widely used dye is especially a suspect. However, natural dyes like *Carotene* are safe food edible colours. For protection of consumer interests, the government of India have passed Prevention of Food Adulteration act (PFA).

18.5 PHEROMONES, SEX ATTRACTANTS

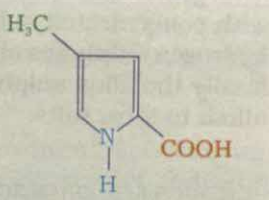
A major drawback with chemical insecticides is their lack of specificity. Non-specificity of insecticides may kill helpful insects, such as honeybees, which aid in pollination. The more specific we make our insect control, the less we will disrupt the environment. Although, in the past, it looked as if specific control was beyond the scope of chemistry, but some developments have shown that it is entirely possible to control populations of certain insects very effectively and specifically using substances known as **pheromones**.

Pheromones provide chemical means of establishing communication. There are sex, trail and defense pheromones to mention a few. One of the most important roles pheromones play is as *sex attractants*. Sex pheromones tell the honeybee which flower to pollinate. The sex pheromones are remarkably powerful. A few hundred molecules may be all that are necessary to invoke a response. In addition to this fascinating parameter, it has been claimed that the sex attractants in some species can attract males from over two miles away. (The sex attractants are usually emitted by the females, although there are some male insects which also produce them). By baiting a trap with a small amount of sex attractant of an insect pest, one can collect all the males in the vicinity. They may then be disposed of or sterilized. Since mating cannot take place, the reproductive cycle is halted and the pest is controlled. The advantages to this method are immediately obvious. It is very specific since, (except in very rare instances), each insect has its own attractant. There is no spraying, hence no pesticide residues. In addition, the concentration of the attractants is so small that there would be no effect on any other species, even indirectly. For example, the gypsy moth attractants, attracts male moths in the area when a trap is baited with only 1×10^{-9}g. Gypsy moths are highly voracious eaters and will completely denude trees if they go unchecked.

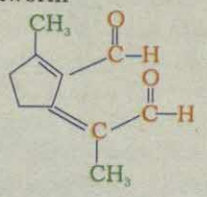
Names and structures of some pheromones



Sex pheromone of the spruce budworm



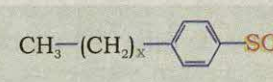
Trail pheromone



Defense pheromone of larvae of Chrysomelid beetle

18.6 DETERGENTS

As a result of high dissolving power, the naturally occurring water always contains dissolved materials, particularly ionic substances. Hard water contains certain metal ions, such as Ca^{2+} and Mg^{2+}. These ions react with soap, (sodium salts of stearic and similar organic acids), to produce a curdy precipitate of calcium and magnesium salts. This precipitate adheres to clothing and blocks the ability of soaps to remove oil and grease from fabrics. Synthetic detergents are very similar to the salts of fatty acids found in soap, except that they are manufactured chemically from materials others than animal fats. Examples include salts called **sodium alkylbenzenesulphonates,** which have the general structure.

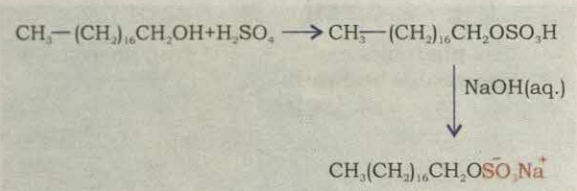


Sodiumalkylbenzenesulphonates

Their advantage over natural soaps is that they work in hard water. The anions of synthetic detergents don't precipitate in the presence of Ca^{2+}/Mg^{2}, so their cleansing action is not affected by hard water.

Types of Detergents

Detergents are mainly classified into three categories, namely anionic, cationic and non-ionic. Long chain alcohols are used in the manufacture of some of the synthetic anionic detergents. The long-chain alcohols are treated with concentrated sulphuric acid to form alkyl hydrogen sulphates of high molecular mass and finally the alkyl sulphates are neutralized with alkali to form salts.

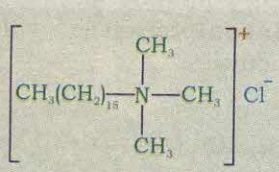


Anionic Detergent

A detergent of the above type is an anionic detergent, named so as a large part of the molecule is an anion. The single anionic detergent in largest use today in household detergents is **alkylbenzene-sulphonate**.

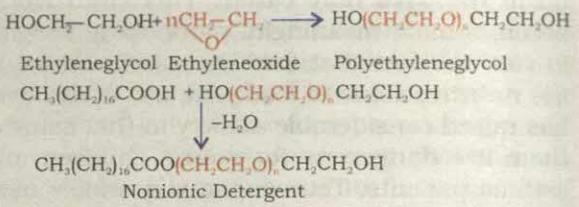
The anionic detergents are also effective in slightly acidic solutions to form an alkyl hydrogen sulphate which is a soluble material, whereas the soaps react with the acidic solutions to form insoluble fatty acids

Second type of detergents are **cationic detergents.** These are mostly acetates or chlorides of quaternary amines. Being more expensive than the anionic detergents they find limited use. Such detergents however, possess germicidal properties and are used quite extensively as germicides. **Cetyltrimethyl-ammonium chloride**, is an example.



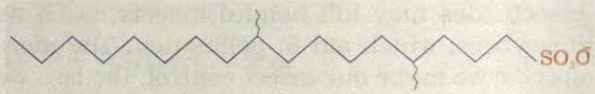
Cationic Detergent

Some of the detergents are **nonionic**, like the esters of high molecular mass formed by reactions between polyethylene glycol and stearic acid.



Some liquid dishwashing detergents are of nonionic type.

In the past many detergents, caused concern for causing pollution in rivers and waterways. The hydrocarbons used earlier for manufacture of detergents had a great deal of branching in the hydrocarbon tail as shown below. This caused pollution.



Detergent molecules associated with branched hydrocarbon tail which is a source of pollution.

The hydrocarbon side chain stops bacteria from attacking and breaking the chains. This results in slow degradation of detergent molecules leading to their accummulation. These days the amount of branching can be kept to a minimum. Unbranched chains are more prone to attack by bacteria so the detergents are more easily biodegraded and pollution is prevented.

18.7 NEW HIGH PERFORMANCE MATERIALS

18.7.1 Carbon Fibres

Carbon fibres are a new breed of high performance materials, which have attracted world-wide attention and hold great promise for the future. This is because of the fact that these fibres are *stronger than steel, stiffer than titanium and lighter than aluminium.* These qualities have placed carbon fibres on top of the list of many novel materials available today. Carbon fibres are produced in a number of ways, and from a variety of starting materials or precursors such as viscose rayon, polyacrylonitrile, pitch, resins, gases such as (methane, and benzene). Their characteristics are strongly influenced by the manufacturing techniques employed.

Carbon fibres *reinforced in a light weight matrix, generally an epoxy resin, polyester resin*

or polyamide, are called Carbon Fibre Reinforced Plastics (CFRP). When the carbon fibres are reinforced in a carbon matrix, they are known as Carbon Fibre Reinforced Carbon (CFRC), commonly known as carbon-carbon composites.

On the basis of the characteristics of carbon fibres, carbon firbre reinforced plastics (CFRP) and carbon fibre reinforced carbons (CFRC), their applications can be broadly classified into three categories:-

1. High technology sector including aerospace, military and nuclear fields.
2. General engineering sector including sports, transportation and chemical fields.
3. Biomedical sector.

In the aerospace sector, the composites are used for aircraft wings, tail parts, helicopter rotor blades, and wing spoilers. The floor decking of air ships is also made from carbon fibre-reinforced composites. Interest in applications involving helicopters continues and it is believed that the first all-composite aircraft to fly will be a helicopter. Helicopter rotor blades made from CFRP not only give better performance but are less expensive than the metal blades.

Carbon fibre in the form of carbon fibre-reinforced carbon commonly known as carbon-carbon composites. The material finds many fascinating applications in heavy and fast jet aircrafts. Breakes made of Carbon-carbon composites perform three to five times better than their steel counterparts.

The high thermal conductivity of carbon fibres enhances the heat dissipation in components such as wall material of nuclear fission reactor, gears, brake pads, bearings, fan blades, automobile parts and other friction related products, further the low coefficient of thermal expansion makes it possible to design structures with zero or very low planar thermal expansion.

Carbon fibres in the form of CFRP find many uses in the area of sports-goods. Very superior specific strength and stiffness, coupled with good fatigue resistance, make them versatile materials for fishing rods, sky poles, tennis and badminton rackets, racing cycle frames, and racing car bodies.

In the biomedical field, carbon fibres have exciting applications, such as components of bone plates, hip joint prostheses, ligaments, and hydraulic motors for artificial heart implants. Activated carbon fibres are finding increasing applications in appliances for water treatment, gas masks, air filters, catalyst carriers for platinum, and so on. Activated carbon fibres in textile form are used in extremely hostile environments. The main advantages of using carbon fibres are that they can be woven in any form and a surface area of as high as 3000 m^2/g can be obtained.

Carbon fibres in India are mainly used in defence sector as nose tips and head shields of missiles (like 'Agni') by DRDO, Hyderabad, and in the aerospace sector by ISRO and other aerospace organizations for producing components parts, nozzles of rockets/missiles.

18.7.2 Ceramics

The term ceramics comes from the Greek word *keramikos* which means burnt stuff, indicating thereby, that desirable properties of these materials are normally achieved through a high-temperature heat treatment process called firing. In the past, the most important materials in this class were the traditional ceramics, prepared from clay, (kaoloinite) a silicate. In the category of traditional ceramics we have porcelain, bricks, tiles, glass and temperature resistant ceramics. Of late, significant progress has been made in understanding the fundamental characterstics of these materials and consequently a new generation of these material has come into existence. The term ceramics has taken on a much broader meaning.

Most ceramic materials fall into an application-classification scheme which is given below.

Clay Products : Porcelain, pottery, tablewares, sanitary fittings, building bricks, tiles and sewer pipes.

Glass Ceramics : Kitchenware

Refractory Materials : Refractory bricks used as furnace linings.

Abrasive Ceramics : Cutting and grinding tools. (familiar examples are silicon and tangsten carbides).

Recently, a family of ceramics have been found to be *superconductors* with high critical temperatures. One such material is yttrium barium copper oxide, which has a critical temperature of about 92 K. New super conducting ceramic materials reported to have even higher critical temperatures have been and are currently being developed. Several of these

materials and their critical temperatures are listed below. The technological potential of these materials is extremely promising as their critical temperatures are above 77 K. Numerous applications of super conducting materials exist. Some of these are:

i) Electrical power transmission.
ii) Magnets for high-energy particle accelerators.
iii) High-speed switching and signal transmission for computer.

High-speed magnetically levitated trains (trains which move on air without rails)

Super Conducting Ceramic Materials and their Critical Temperatures.

Material	Elements Present In the material	Critical Temp./K
$YBa_2Cu_3O_7$	Y, Ba, Cu, O	92
$Bi_2Sr_2Ca_2Cu_3O_{10}$	Bi, Sr, Ca, Cu, O	110
$Tl_2Ba_2Ca_2Cu_3O_{10}$	Tl, Ba, Ca, Cu, O	125
$HgBa_2Ca_2Cu_2O_8$	Hg, Ba, Ca, Cu, O	153

18.7.3 Microalloys

We know from our experiences that 24 karat gold is traditionally not used to manufacture jewellery as it cannot withstand everyday wear. To overcome this difficulty, recently a number of microalloyed high karat gold qualities have been marketed with a gold content of 99.55 per cent or even higher. These microalloys are found to posses improved hardness and strength. This makes it possible for the jewellers to use in the trade 24 karat hallmark and at the same time to retain its finish and structure in everyday use. In some of the cases the microalloyed gold is found to show physical properties very similar to platinum.

Steel and steel alloys are familiar materials to us. Now microalloyed steels have started engaging the attention of researchers. Microalloyed steels posses excellent combinations of strength and toughness, formability and weldability. The usual microalloyed steels contain niobium, titanium and vanadium. In some cases microalloyed materials have shown excellent resistance to deformation. These materials have been found to retain their shape even under very high loads.

18.8 ROCKET PROPELLANTS

The idea of rockets is not new, for example, the Britishers employed rockets against United States forces during the war of 1812 with some measure of success. Modern rocketry came into being towards the close of 19th Century. K.E. Tsiolkovskii in Russia, R.H. Goddard in USA, and H. Oberth in Germany were the pioneers. Goddard's work during the 1920's and '30s established both theoretically and experimentally the practicability of the use of liquid propelled rocket. Since independence, India too is making a commendable progress in the area of space research programme. We know about the successful launching of India's first satellite vehicle, SLV-3, which heralded the beginning of India's space programmes.

Rocket motors are used both in space vehicle and in offensive weapons such as missiles. The propulsion system in most space vehicles consists of rocket engines powered by what are known as *chemical propellants*. A propellant is a combination of an oxidizer and a fuel, which when ignited, undergoes combustion to release great quantities of hot gases. The passage of gases through the nozzle of the rocket motor, provides the necessary thrust for the rocket to move forward.

This effect is similar to that of the flying of a fully blown balloon when its air is allowed to escape through a narrow neck. The function of a rocket propellant is similar to that of petrol in a motor car except that in the later case, the oxygen needed for burning the fuel is taken from the atmospheric air.

Depending upon their physical state, propellants are classified into the following types: (a) *solid propellants*, (b) *liquid propellants* and (c) *hybrid propellants*.

The most common and widely used solid propellant is a **composite propellant** which is a blend of a polymeric binder such as polyurethane or polybutadiene as fuel and ammonium perchlorate as oxidizer along with some additives (in particular, a metal such as aluminium or magnesium in finely divided form) to modify the performance of the propellant. Another type of solid propellant is known as **double-base propellant** which mainly consists of nitroglycerine and nitrocellulose. Nitrocellulose gels in nitroglycerine sets in as a solid mass. Solid propellants, once ignited, will

burn with a pre-determined rate and do not have the start and stop capability.

Liquid propellants consist of a combination of an oxidizer such as liquid oxygen, nitrogen tetraoxide (N_2O_4) or nitric acid and a fuel such as kerosene, alcohol, hydrazine or liquid hydrogen. These biliquid propellants, in general, give higher thrusts than solid propellants and the thrust can be controlled by switching on and off the flow of the propellant.

Monopropellants are liquid propellants wherein a single chemical compound on decomposition or ignition gives out hot gases. Examples of this type are hydrazine, methylnitrate, nitromethane and hydrogen peroxide. Except hydrazine, the other compounds mentioned contain both the oxidizer and the fuel elements in the same molecule. *Liquid propellant systems are usually classified as either storable or cryogenic. The cyrogenic systems generally show high performance.*

It is also possible to use **hybrid rocket propellant**, which usually consists of a solid fuel and a liquid oxidizer (e.g., liquid N_2O_4 + acrylic rubber)

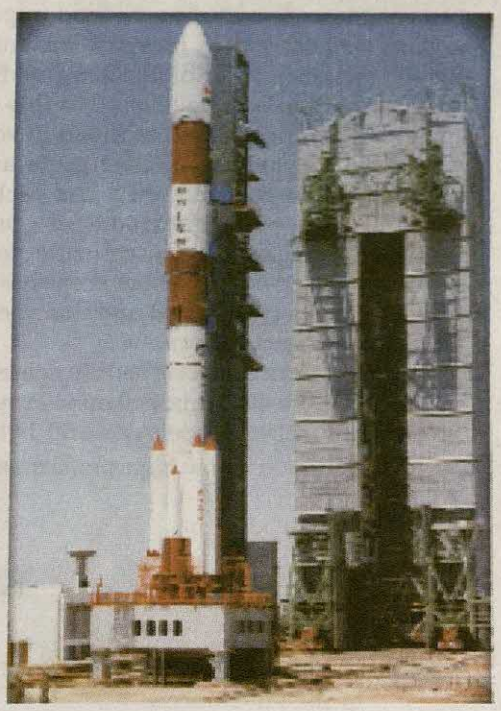
The prime criterion of rocket propellant performance is specific impulse, which measures kinetic energy producing ability of the propellant. The fundamental equation for specific impulse, I_s is

$$I_s = \frac{1}{g}\sqrt{\left(\frac{2\gamma}{\gamma-1}\right)\left(\frac{gRT_c}{M}\right)\left(1-\frac{p_c}{p_e}\right)^{\frac{\gamma-1}{\gamma}}}$$

where γ = ratio of specific heat at constant pressure to specific heat at constant volume.
R = gas constant
T_c = combustion chamber temperature.
M = average molecular mass of exhaust products
p_e = external pressure
p_c = chamber pressure

Examination of the above equation reflects that the conditions favouring high specific impulse are high chamber temperature and pressure, low molecular mass of exhaust products, and low external pressure. The higher the temperature and pressure achieved in the chamber, the higher the kinetic energy of the gases escaping through the nozzle.

In our country, the interest of the Indian Space Research Organization (ISRO) has been to launch, and utilize two classes of satellites – remote sensing satellites and communication satellites. The Polar Satellite Launch Vehicle (PSLV) is a remote sensing satellite. You may be interested to know that India, so far, has launched several space vehicles using various rocket propellants. PSLV – C4 India's latest vehicle which took flight on 12th September, 2002 has been given the name METSAT MISSION. It is a four stage vehicle. The first stage is one of the largest solid propellant boosters in the world and carries 138 tonne of Hydroxyl Terminated Polybutadiene (HTPB) based propellant. The second stage employs indigenously built VIKAS engine and carries 40 tonne of liquid propellant unsymmertrical dimethylhydrazine (UDMH) as fuel and nitrogen tetraoxide (N_2O_4) as oxidizer. The third stage again uses 7.6 tonne of HTPB-based solid propellant. The fourth and the terminal stage of PSLV – C4 has a twin engine configuration using liquid propellant. Each engine uses 2.5 tonne of mono-methyl hydrazine as fuel and mixed oxides of nitrogen as oxidizer.



Polar Satellite Launch Vehicle.

SUMMARY

Chemistry is essentially the study of materials and the development of new materials for the betterment of humanity. A drug is a chemical agent, which affects human metabolism and provides cure from ailment. Drug chemistry centres around arresting microbes/destroying microbes, preventing the body from various infectious diseases, releasing mental stress etc. Thus, drugs like analgesics, antibiotics, antiseptics, disinfectants, antacids and tranquilizers are used with specific purpose. Of late, to check the explosion of population growth, antifertility drugs have also become prominent part of our life. In using all these drugs, the principle of safety is the hall mark.

Dyeing involves imparting adequate and fast colour to the fabric. For this purpose, acidic, basic, azo, disperse, fibre reactive, vat and mordant dyes are used. Use of the dye depends on the nature of the fibre to be dyed. Cosmetics are used to enhance the body appeal. Whereas facial creams tend to keep the face clean and smooth, perfumes essentially are used to impart appealing fragrance. Talcum powders and deodorants arrest the bacterial decay arising from perspiration.

Carbon fibres a form of carbon, are used to design composites, which find use in constructing sports articles and certain space craft parts. Ceramics were known to mankind since ancient times and today new ceramics are being developed. Superconducting ceramics which are compounds of certain metals with oxygen have been engaging the attention of scientists. Micro-alloys is a new term in the area of material science and it has been possible to achieve comparable tenstile strength of alloys with the addition of only small amount of certain specific metals to the host metal.

Food additives such as preservatives, sweetening agents, antioxidants and edible colours are added to the food to make it attractive and platable. Antioxidants arrest the aging process of the food by preventing the food stuff from spoilage. The two most versatile antioxidants used for this purpose are butylated hydroxy toluene (BHT) and butylated hydroxy anisole (BHA). Saccharin is a versatile sweetening agent used as food additive. Preservatives are added to the food to prevent spoilage due to microbial growth. Certain organic acid derivatives figure prominently as preservatives, of which sodium benzoate is the common material. Edible colours added to the food articles enhance their visual appeal; special care needs to be taken that this addition must be safe for health.

Detergents these days are much in vogue and get preference over soaps because they work even in hard water. Detergents are classified into three main categories namely: anionic, cationic and nonionic and each category has its specific uses. Detergents with straight chain of hydrocarbons are preferred over branched chain as the latter are nonbiodegradable and consequently present environmental pollution. Pheromones sex attractants are used to combat problems arising out of the use of insecticides. Pheromones, have highly specific appeal and this specificity of their action makes them safe agents to be used for insect control.

Rocket motors are used both in space vehicles and in missiles. Here rocket engines are powered by chemical propellants. Propellants are grouped into three categories: solid propellants, liquid propellants and hybrid propellants. The cryogenic liquid propellant systems generally show high performance by providing greater thrust.

EXERCISES

18.1 How are antiseptics distinguished from disinfectants? Give two examples of each of the substances.

18.2 What is an antibiotic? Give the name of the first antibiotic discovered.

18.3 List two major classes of antibiotics with an example of each class.

18.4 What are antacids? List some of the compounds, which are used as antacids.

18.5 Describe the following with suitable examples:
(i) Tranquilizers (ii) Antifertility drugs (iii) Antihistamines.

18.6 Present a scheme of classification of dyes based on their application.

18.7 Give an examples of : (i) Tripenylmethane dye (ii) Azo dye (iii) Anthraquinone dye

18.8 What is a mordant dye ? How is it applied to the fabric?

18.9 Bring out the essential point of difference between acidic dyes and basic dyes.

18.10 What are the essential components of a talcum powder? What is the role of boric acid in talcum powder?

18.11 What are deodorants and what is their specific role in cosmetics.

18.12 What are the essential components of a perfume ? How does the function of a perfume differ from cream?

18.13 What are carbon fibres? How are they designed? Write two important uses of carbon fibres.

18.14 List various type of ceramics and their uses.

18.15 What are superconducting ceramics? Write some uses of superconductor ceramics.

18.16 Write a brief note on micro-alloys.

18.17 Describe the following with suitable examples
(i) Preservative (ii) Artificial sweeteners
(iii) Antioxidants (iv) Edible colours

18.18 What are detergents? Give their scheme of classification. Why are detergents preferred over soaps?

18.19 What are biodegradable and nonbiodegradable detergents? What are the consequences of using latter class of detergents?

18.20 What are pheromones? Why are pheromones said to be action specific agents?

18.21 What is a propellant? How are various rocket propellants classified?

18.22 What propellants have been used in PSLV – C4 rocket?

18.23 Describe the following with examples:
(i) Doube-base propellant (ii) Biliquid propellant
(iii) Monoliquid propellant (iv) Hybrid propellant

18.24 Discuss the role of redox phenomenon in the context of rocket propellants.

Appendix I

Thermodynamic Data at 298 K

INORGANIC SUBSTANCES

Substance	Enthalpy of formation, $\Delta_f H^\ominus$ / kJ mol^{-1}	Gibbs Energy of formation, $\Delta_f G^\ominus$ / kJ mol^{-1}	Entropy,* $S^\ominus$ / J K^{-1} mol^{-1}
Aluminium			
Al(s)	0	0	28.33
Al^{3+}(aq)	- 524.7	–481.2	–321.7
Al_2O_3(s)	–1675.7	–1582.3	50.92
$Al(OH)_3$(s)	–1276	—	—
$AlCl_3$(s)	–704.2	–628.8	110.67
Antimony			
SbH_3(g)	145.11	147.75	232.78
$SbCl_3$(g)	–313.8	–301.2	337.80
$SbCl_5$(g)	–394.34	–334.29	401.94
Arsenic			
As(s), gray	0	0	35.1
As_2S_3(s)	–169.0	–168.6	163.6
AsO_4^{3-}(aq)	–888.14	–648.41	–162.8
Barium			
Ba(s)	0	0	62.8
Ba^{2+}(aq)	–537.64	–560.77	9.6
BaO(s)	–553.5	–525.1	70.42
$BaCO_3$(s)	–1216.3	–1137.6	112.1
$BaCO_3$(aq)	–1214.78	–1088.59	–47.3
Boron			
B(s)	0	0	5.86
B_2O_3(s)	–1272.8	–1193.7	53.97
BF_3(g)	–1137.0	–1120.3	254.12
Bromine			
Br_2(l)	0	0	152.23
Br_2(g)	30.91	3.11	245.46
Br(g)	111.88	82.40	175.02
Br^-(aq)	–121.55	–103.96	82.4
HBr(g)	–36.40	–53.45	198.70
BrF_3(g)	–255.60	–229.43	292.53
Calcium			
Ca(s)	0	0	41.42
Ca(g)	178.2	144.3	154.88
Ca^{2+}(aq)	–542.83	–553.58	–53.1

(continued)

Substance	Enthalpy of formation, $\Delta_f H^\ominus$ / kJ mol^{-1}	Gibbs Energy of formation, $\Delta_f G^\ominus$ / kJ mol^{-1}	Entropy,* $S^\ominus$ /J K^{-1} mol^{-1}
Calcium (continued)			
CaO(s)	–635.09	–604.03	39.75
$Ca(OH)_2$(s)	–986.09	–898.49	83.39
$Ca(OH)_2$(aq)	–1002.82	–868.07	–74.5
$CaCO_3$(s), calcite	–1206.9	–1128.8	92.9
$CaCO_3$(s), aragonite	–1207.1	–1127.8	88.7
$CaCO_3$(aq)	–1219.97	–1081.39	–110.0
CaF_2(s)	–1219.6	–1167.3	68.87
CaF_2(aq)	–1208.09	–1111.15	–80.8
$CaCl_2$(s)	–795.8	–748.1	104.6
$CaCl_2$(aq)	–877.1	–816.0	59.8
$CaBr_2$(s)	–682.8	–663.6	130
CaC_2(s)	–59.8	–64.9	69.96
CaS(s)	–482.4	–477.4	56.5
$CaSO_4$(s)	–1434.11	–1321.79	106.7
$CaSO_4$(aq)	–1452.10	–1298.10	–33.1
*Carbon***			
C(s), graphite	0	0	5.740
C(s), diamond	1.895	2.900	2.377
C(g)	716.68	671.26	158.10
CO(g)	–110.53	–137.17	197.67
CO_2(g)	–393.51	–394.36	213.74
CO_3^{2-}(aq)	–677.14	–527.81	–56.9
CCl_4(l)	–135.44	–65.21	216.40
CS_2(l)	89.70	65.27	151.34
HCN(g)	135.1	124.7	201.78
HCN(l)	108.87	124.97	112.84
Cerium			
Ce(s)	0	0	72.0
Ce^{3+}(aq)	–696.2	–672.0	–205
Ce^{4+}(aq)	–537.2	–503.8	–301
Chlorine			
Cl_2(g)	0	0	223.07
Cl(g)	121.68	105.68	165.20
Cl^-(aq)	–167.16	–131.23	56.5
HCl(g)	–92.31	–95.30	186.91
HCl(aq)	–167.16	–131.23	56.5
Copper			
Cu(s)	0	0	33.15
Cu^+(aq)	71.67	49.98	40.6
Cu^{2+}(aq)	64.77	65.49	–99.6
Cu_2O(aq)	–168.6	–146.0	93.14
CuO(s)	–157.3	–129.7	42.63
$CuSO_4$(s)	–771.36	–661.8	109
$CuSO_4.5H_2O$(s)	–2279.7	–1879.7	300.4

** For organic compounds, a separate table is provided in continuation.

(continued)

Substance	Enthalpy of formation, $\Delta_f H^\ominus$ / kJ mol^{-1}	Gibbs Energy of formation, $\Delta_f G^\ominus$ / kJ mol^{-1}	Entropy,* $S^\ominus$ /J K^{-1} mol^{-1}
Deuterium			
$D_2(g)$	0	0	144.96
$D_2O(g)$	–249.20	–234.54	198.34
$D_2O(l)$	–294.60	–243.44	75.94
Fluorine			
$F_2(g)$	0	0	202.78
$F^-(aq)$	–332.63	–278.79	–13.8
HF(g)	–271.1	–273.2	173.78
HF(aq)	–332.63	–278.79	–13.8
Hydrogen (see also Deuterium)			
$H_2(g)$	0	0	130.68
H(g)	217.97	203.25	114.71
$H^+(aq)$	0	0	0
$H_2O(l)$	–285.83	–237.13	69.91
$H_2O(g)$	–241.82	–228.57	188.83
$H_2O_2(l)$	–187.78	–120.35	109.6
$H_2O_2(aq)$	–191.17	–134.03	143.9
Iodine			
$I_2(s)$	0	0	116.14
$I_2(g)$	62.44	19.33	260.69
$I^-(aq)$	–55.19	–51.57	111.3
HI(g)	26.48	1.70	206.59
Iron			
Fe(s)	0	0	27.28
$Fe^{2+}(aq)$	–89.1	–78.90	–137.7
$Fe^{3+}(aq)$	–48.5	–4.7	–315.9
$Fe_3O_4(s)$, magnetite	–1118.4	–1015.4	146.4
$Fe_2O_3(s)$, haematite	–824.2	–742.2	87.40
FeS(s,α)	–100.0	–100.4	60.29
FeS(aq)	—	6.9	—
$FeS_2(s)$	–178.2	–166.9	52.93
Lead			
Pb(s)	0	0	64.81
$Pb^{2+}(aq)$	–1.7	–24.43	10.5
$PbO_2(s)$	–277.4	–217.33	68.6
$PbSO_4(s)$	–919.94	–813.14	148.57
$PbBr_2(s)$	–278.7	–261.92	161.5
$PbBr_2(aq)$	–244.8	–232.34	175.3
Magnesium			
Mg(s)	0	0	32.68
Mg(g)	147.70	113.10	148.65
$Mg^{2+}(aq)$	–466.85	–454.8	–138.1
MgO(s)	–601.70	–569.43	26.94
$MgCO_3(s)$	–1095.8	–1012.1	65.7
$MgBr_2(s)$	–524.3	–503.8	117.2

(continued)

Substance	Enthalpy of formation, $\Delta_f H^\ominus$ / kJ mol^{-1}	Gibbs Energy of formation, $\Delta_f G^\ominus$ / kJ mol^{-1}	Entropy,* $S^\ominus$ /J K^{-1} mol^{-1}
Mercury			
Hg(1)	0	0	76.02
Hg(g)	61.32	31.82	174.96
HgO(s)	–90.83	–58.54	70.29
Hg_2Cl_2(s)	–265.22	–210.75	192.5
Nitrogen			
N_2(g)	0	0	191.61
NO(g)	90.25	86.55	210.76
N_2O(g)	82.05	104.20	219.85
NO_2(g)	33.18	51.31	240.06
N_2O_4(g)	9.16	97.89	304.29
HNO_3(1)	–174.10	–80.71	155.60
HNO_3(aq)	–207.36	–111.25	146.4
NO_3^- (aq)	–205.0	–108.74	146.4
NH_3(g)	–46.11	–16.45	192.45
NH_3(aq)	–80.29	–26.50	111.3
NH_4^+ (aq)	–132.51	–79.31	113.4
NH_2OH(s)	–114.2	—	—
HN_3(g)	294.1	328.1	238.97
N_2H_4(1)	50.63	149.34	121.21
NH_4NO_3(s)	–365.56	–183.87	151.08
NH_4Cl(s)	–314.43	–202.87	94.6
NH_4ClO_4(s)	–295.31	–88.75	186.2
Oxygen			
O_2(g)	0	0	205.14
O_3(g)	142.7	163.2	238.93
OH^-(aq)	–229.99	–157.24	–10.75
Phosphorus			
P(s), white	0	0	41.09
P_4(g)	58.91	24.44	279.98
PH_3(g)	5.4	13.4	210.23
P_4O_{10}(s)	–2984.0	–2697.0	228.86
H_3PO_3(aq)	–964.8	—	—
H_3PO_4(1)	–1266.9	—	—
H_3PO_4(aq)	–1277.4	–1018.7	—
PCl_3(1)	–319.7	–272.3	217.18
PCl_3(g)	–287.0	–267.8	311.78
PCl_5(g)	–374.9	–305.0	364.6
Potassium			
K(s)	0	0	64.18
K(g)	89.24	60.59	160.34
K^+(aq)	–252.38	–283.27	102.5
KOH(s)	–424.76	–379.08	78.9
KOH(aq)	–482.37	–440.50	91.6
KF(s)	–567.27	–537.75	66.57

(continued)

Substance	Enthalpy of formation, $\Delta_f H^\ominus$ / kJ mol^{-1}	Gibbs Energy of formation, $\Delta_f G^\ominus$ / kJ mol^{-1}	Entropy,* $S^\ominus$ / J K^{-1} mol^{-1}
Potassium (continued)			
KCl(s)	–436.75	–409.14	82.59
KBr(s)	–393.80	–380.66	95.90
KI(s)	–327.90	–324.89	106.32
$KClO_3$(s)	–397.73	–296.25	143.1
$KClO_4$(s)	–432.75	–303.09	151.0
K_2S(s)	–380.7	–364.0	105
K_2S(aq)	–471.5	–480.7	190.4
Silicon			
Si(s)	0	0	18.83
SiO_2(s,α)	–910.94	–856.64	41.84
Silver			
Ag(s)	0	0	42.55
Ag^+(aq)	105.58	77.11	72.68
Ag_2O(s)	–31.05	–11.20	121.3
AgBr(s)	–100.37	–96.90	107.1
AgBr(aq)	–15.98	–26.86	155.2
AgCl(s)	–127.07	–109.79	96.2
AgCl(aq)	–61.58	–54.12	129.3
AgI(s)	–61.84	–66.19	115.5
AgI(aq)	50.38	25.52	184.1
$AgNO_3$(s)	–124.39	–33.41	140.92
Sodium			
Na(s)	0	0	51.21
Na(g)	107.32	76.76	153.71
Na^+(aq)	–240.12	–261.91	59.0
NaOH(s)	–425.61	–379.49	64.46
NaOH(aq)	–470.11	–419.15	48.1
NaCl(s)	–411.15	–384.14	72.13
NaCl(aq)	–407.3	–393.1	115.5
NaBr(s)	–361.06	–348.98	86.82
NaI(s)	–287.06	–286.06	98.53
$NaHCO_3$(s)	–947.7	–851.9	102.1
Na_2CO_3(s)	–1130.9	–1047.7	136.0
Sulphur			
S(s), rhombic	0	0	31.80
S(s), monoclinic	0.33	0.1	32.6
S^{2-}(aq)	33.1	85.8	–14.6
SO_2(g)	–296.83	–300.19	248.22
SO_3(g)	–395.72	–371.06	256.76
H_2SO_4(l)	–813.99	–690.00	156.90
H_2SO_4(aq)	–909.27	–744.53	20.1
SO_4^{2-}(aq)	–909.27	–744.53	20.1
H_2S(g)	–20.63	–33.56	205.79
H_2S(aq)	–39.7	–27.83	121
SF_6(g)	–1209	–1105.3	291.82

(continued)

Substance	Enthalpy of formation, $\Delta_f H^\ominus$ / kJ mol^{-1}	Gibbs Energy of formation, $\Delta_f G^\ominus$ / kJ mol^{-1}	Entropy,* $S^\ominus$ /J K^{-1} mol^{-1}
Tin			
Sn(s), white	0	0	51.55
Sn(s), gray	-2.09	0.13	44.14
SnO(s)	-285.8	-256.9	56.5
SnO_2(s)	-580.7	-519.6	52.3
Zinc			
Zn(s)	0	0	41.63
Zn^{2+}(aq)	-153.89	-147.06	-112.1
ZnO(s)	-348.28	-318.30	43.64
Zn(g)	+130.73	+95.14	160.93

*The entropies of individual ions in solution are determined by setting the entropy of H^+ in water equal to 0 and then defining the entropies of all other ions relative to this value; hence a negative entropy is one that is lower than the entropy of H^+ in water.

ORGANIC COMPOUNDS

Substance	Enthalpy of combustion, $\Delta_c H^\ominus$ / kJ mol^{-1}	Enthalpy of formation, $\Delta_f H^\ominus$ / kJ mol^{-1}	Gibbs Energy of formation, $\Delta_f G^\ominus$ / kJ mol^{-1}	Entropy, $S^\ominus$ /J K^{-1} mol^{-1}
Hydrocarbons				
CH_4(g), methane	-890	-74.81	-50.72	186.26
C_2H_2(g), ethyne (acetylene)	-1300	226.73	209.20	200.94
C_2H_4(g), ethene(ethylene)	-1411	52.26	68.15	219.56
C_2H_6(g), ethane	-1560	-84.68	-32.82	229.60
C_3H_6(g), propene (propylene)	-2058	20.42	62.78	266.6
C_3H_6(g), cyclopropane	-2091	53.30	104.45	237.4
C_3H_8(g), propane	-2220	-103.85	-23.49	270.2
C_4H_{10}(g), butane	-2878	-126.15	-17.03	310.1
C_5H_{12}(g), pentane	-3537	-146.44	-8.20	349
C_6H_6(l), benzene	-3268	49.0	124.3	173.3
C_6H_6(g)	-3302	—	—	—
C_7H_8(l), toluene	-3910	12.0	113.8	221.0
C_7H_8(g)	-3953	—	—	—
C_6H_{12}(l), cyclohexane	-3920	-156.4	26.7	204.4
C_6H_{12}(g),	-3953	—	—	—
C_8H_{18}(l), octane	-5471	-249.9	6.4	358
Alcohols and phenols				
CH_3OH(l), methanol	-726	-238.86	-166.27	126.8
CH_3OH(g)	-764	-200.66	-161.96	239.81
C_2H_5OH(l), ethanol	-1368	-277.69	-174.78	160.7
C_2H_5OH(g)	-1409	-235.10	-168.49	282.70
C_6H_5OH(s), phenol	-3054	-164.6	-50.42	144.0

(continued)

Substance	Enthalpy of combustion, $\Delta_c H^\ominus$ / kJ mol^{-1}	Enthalpy of formation, $\Delta_f H^\ominus$ / kJ mol^{-1}	Gibbs Energy of formation, $\Delta_f G^\ominus$ / kJ mol^{-1}	Entropy, $S^\ominus$ /J K^{-1} mol^{-1}
Carboxylic acid				
HCOOH(l), formic acid	–255	–424.72	–361.35	128.95
CH_3COOH(l), acetic acid	–875	–484.5	–389.9	159.8
CH_3COOH (aq)	—	–485.76	–396.64	86.6
$(COOH)_2$(s), oxalic acid	–254	–827.2	–697.9	120
C_6H_5COOH(s), benzoic acid	–3227	–385.1	–245.3	167.6
Aldehydes and ketones				
HCHO(g), methanal (formaldehyde)	–571	–108.57	–102.53	218.77
CH_3CHO(l), ethanal (acetaldehyde)	–1166	–192.30	–128.12	160.2
CH_3CHO(g)	–1192	–166.19	–128.86	250.3
CH_3COCH_3(l), propanone (acetone)	–1790	–248.1	–155.4	200
Sugars				
$C_6H_{12}O_6$(s), glucose	–2808	–1268	–910	212
$C_6H_{12}O_6$(aq)	—	—	–917	—
$C_6H_{12}O_6$(s), fructose	–2810	–1266	—	—
$C_{12}H_{22}O_{11}$(s), sucrose	–5645	–2222	–1545	360
Nitrogen compounds				
$CO(NH_2)_2$(s), urea	–632	–333.51	–197.33	104.60
$C_6H_5NH_2$(l), aniline	–3393	31.6	149.1	191.3
NH_2CH_2COOH(s), glycine	–969	–532.9	–373.4	103.51
CH_3NH_2(g), methylamine	–1085	–22.97	32.16	243.41

APPENDIX II

Standard potentials at 298 K in electrochemical order

Reduction half-reaction	E°/V	Reduction half-reaction	E°/V
$H_4XeO_6 + 2H^+ + 2e^- \longrightarrow XeO_3 + 3H_2O$	+3.0	$Cu^+ + e^- \longrightarrow Cu$	+0.52
$F_2 + 2e^- \longrightarrow 2F^-$	+2.87	$NiOOH + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$	+0.49
$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$	+2.07	$Ag_2CrO_4 + 2e^- \longrightarrow 2Ag + CrO_4^{2-}$	+0.45
$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$	+2.05	$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	+0.40
$Ag^+ + e^- \longrightarrow Ag^+$	+1.98	$ClO_4^- + H_2O + 2e^- \longrightarrow ClO_3^- + 2OH^-$	+0.36
$Co^{3+} + e^- \longrightarrow Co^{2+}$	+1.81	$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$	+0.36
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	+1.78	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Au^+ + e^- \longrightarrow Au$	+1.69	$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+0.27
$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}$	+1.67	$AgCl + e^- \longrightarrow Ag + Cl^-$	+0.27
$2HClO + 2H^+ + 2e^- \longrightarrow Cl_2 + 2H_2O$	+1.63	$Bi^{3+} + 3e^- \longrightarrow Bi$	+0.20
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	+1.61	$SO_4^{2-} + 4H^+ + 2e^- \longrightarrow H_2SO_3 + H_2O$	+0.17
$2HBrO + 2H^+ + 2e^- \longrightarrow Br_2 + 2H_2O$	+1.60	$Cu^{2+} + e^- \longrightarrow Cu^+$	+0.16
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.51	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.15
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$	+1.51	$AgBr + e^- \longrightarrow Ag + Br^-$	+0.07
$Au^{3+} + 3e^- \longrightarrow Au$	+1.40	$Ti^{4+} + e^- \longrightarrow Ti^{3+}$	0.00
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36	$2H^+ + 2e^- \longrightarrow H_2$	0.0 by definition
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33	$Fe^{3+} + 3e^- \longrightarrow Fe$	–0.04
$O_3 + H_2O + 2e^- \longrightarrow O_2 + 2OH^-$	+1.24	$O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^-$	–0.08
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.23	$Pb^{2+} + 2e^- \longrightarrow Pb$	–0.13
$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + 2H_2O$	+1.23	$In^+ + e^- \longrightarrow In$	–0.14
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.23	$Sn^{2+} + 2e^- \longrightarrow Sn$	–0.14
$Pt^{2+} + 2e^- \longrightarrow Pt$	+1.20	$AgI + e^- \longrightarrow Ag + I^-$	–0.15
$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.09	$Ni^{2+} + 2e^- \longrightarrow Ni$	–0.23
$Pu^{4+} + e^- \longrightarrow Pu^{3+}$	+0.97	$V^{3+} + e^- \longrightarrow V^{2+}$	–0.26
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+0.96	$Co^{2+} + 2e^- \longrightarrow Co$	–0.28
$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+0.92	$In^{3+} + 3e^- \longrightarrow In$	–0.34
$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$	+0.89	$Tl^+ + e^- \longrightarrow Tl$	–0.34
$Hg^{2+} + 2e^- \longrightarrow Hg$	+0.86	$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$	–0.36
$NO_3^- + 2H^+ + e^- \longrightarrow NO_2 + H_2O$	+0.80	$Ti^{3+} + e^- \longrightarrow Ti^{2+}$	–0.37
$Ag^+ + e^- \longrightarrow Ag$	+0.80	$Cd^{2+} + 2e^- \longrightarrow Cd$	–0.40
$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$	+0.79	$In^{2+} + e^- \longrightarrow In^+$	–0.40
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77	$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	–0.41
$BrO^- + H_2O + 2e^- \longrightarrow Br^- + 2OH^-$	+0.76	$Fe^{2+} + 2e^- \longrightarrow Fe$	–0.44
$Hg_2SO_4 + 2e^- \longrightarrow 2Hg + SO_4^{2-}$	+0.62	$In^{3+} + 2e^- \longrightarrow In^+$	–0.44
$MnO_4^{2-} + 2H_2O + 2e^- \longrightarrow MnO_2 + 4OH^-$	+0.60	$S + 2e^- \longrightarrow S^{2-}$	–0.48
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	+0.56	$In^{3+} + e^- \longrightarrow In^{2+}$	–0.49
$I_2 + 2e^- \longrightarrow 2I^-$	+0.54	$U^{4+} + e^- \longrightarrow U^{3+}$	–0.61
$I_3^- + 2e^- \longrightarrow 3I^-$	+0.53	$Cr^{3+} + 3e^- \longrightarrow Cr$	–0.74
		$Zn^{2+} + 2e^- \longrightarrow Zn$	–0.76

(continued)

Appendix II continued

Reduction half-reaction	$E^\ominus$/V	Reduction half-reaction	$E^\ominus$/V
$Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-$	–0.81	$La^{3+} + 3e^- \longrightarrow La$	–2.52
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	–0.83	$Na^+ + e^- \longrightarrow Na$	–2.71
$Cr^{2+} + 2e^- \longrightarrow Cr$	–0.91	$Ca^{2+} + 2e^- \longrightarrow Ca$	–2.87
$Mn^{2+} + 2e^- \longrightarrow Mn$	–1.18	$Sr^{2+} + 2e^- \longrightarrow Sr$	–2.89
$V^{2+} + 2e^- \longrightarrow V$	–1.19	$Ba^{2+} + 2e^- \longrightarrow Ba$	–2.91
$Ti^{2+} + 2e^- \longrightarrow Ti$	–1.63	$Ra^{2+} + 2e^- \longrightarrow Ra$	–2.92
$Al^{3+} + 3e^- \longrightarrow Al$	–1.66	$Cs^+ + e^- \longrightarrow Cs$	–2.92
$U^{3+} + 3e^- \longrightarrow U$	–1.79	$Rb^+ + e^- \longrightarrow Rb$	–2.93
$Sc^{3+} + 3e^- \longrightarrow Sc$	–2.09	$K^+ + e^- \longrightarrow K$	–2.93
$Mg^{2+} + 2e^- \longrightarrow Mg$	–2.36	$Li^+ + e^- \longrightarrow Li$	–3.05
$Ce^{3+} + 3e^- \longrightarrow Ce$	–2.48		

APPENDIX III

Answers to Some Selected Problems

UNIT 1

1.3 10^{-7} m
1.4 7.95×10^{-40} m
1.6 2.6×10^{-39} m s^{-1}
1.7 9.58×10^{-10} m

UNIT 2

2.9 107.8 u
2.11 14.29 nm
2.13 8.97 g cm^{-3}
2.14 1.29×10^{24} mol^{-1}
2.15 Ni^{2+} = 96% and Ni^{3+} = 4%
2.16 578 pm
2.17 7.53×10^{-2} nm
2.18 0.115 nm
2.29 (a) 354 pm (b) 2.26×10^{22} unit cells
2.30 6.02×10^{18} cation vacancies mol^{-1}
2.31 269 pm
2.32 6.09×10^{23} mol^{-1}

UNIT 3

3.4 16.23 M
3.5 0.617 *m*, 0.01 and 0.99, 0.67 M
3.6 157.8 mL
3.7 32% and 68%
3.8 17.95 *m* and 8.70 M
3.9 ~ 15×10^{-4} g, 1.25×10^{-4} *m*
3.15 41.35 g mol^{-1}
3.16 73.08 kPa
3.17 12.08 kPa
3.18 8 g
3.19 34 g mol^{-1}, 3.4 kPa
3.20 269.07 K
3.21 A = 25.58 u and B = 42.64 u
3.22 0.061M

UNIT 4

4.11 (i) +84.4 J K mol^{-1} (ii) –84.4 mol^{-1} JK^{-1}
4.12 –270.1 JK^{-1} mol^{-1}
4.15 (a) –748.1 kJ mol^{-1}, (b) 58.54 kJ mol^{-1}, (c) –301.39 kJ mol^{-1}
4.16 $\Delta_r G^\ominus$ = – 702 kJ mol^{-1}, 97% of Gibbs energy can be converted to electrical work.
4.17 K_p = 2.6
4.19 $\Delta_r G^\ominus$ at 298 K is –69.80 kJ mol^{-1} and, therefore, reaction is spontaneous
4.20 $\Delta_r G^\ominus$ = –24.1 kJ mol^{-1}, K_p = 9.75, p_{CO_2} = 9.75 bar
4.23 (a) $\Delta_r G^\ominus$ = – 800 kJ mol^{-1}
(b) $\Delta_r G^\ominus$ = –56.37 kJ mol^{-1}
4.24 383 K

UNIT 5

5.3 124.0 S cm^2 mol^{-1}
5.4 3 F, 2F, 5F
5.5 1F, 4.44F
5.6 2F, 1F
5.7 1.803 g
5.8 14.40 min, Copper 0.427g, Zinc 0.437 g
5.14 (i) $E^{\ominus} = 0.34V$, $\Delta_r G^{\ominus} = -196.86$ kJ mol^{-1}, $K = 3.16 \times 10^{34}$
(ii) $E^{\ominus} = 0.03V$, $\Delta_r G^{\ominus} = -2.895$ kJ mol^{-1}, $K = 3.2$
5.15 (i) 2.68 V, (ii) 0.53 V, (iii) 0.08 V, (iv) –1.315 V
5.16 1.105 V
5.17 0.219 cm^{-1}
5.19 1.85×10^{-5}

UNIT 6

6.2 (i) 8.0×10^{-9} M^{-2} s^{-1} (ii) 3.89×10^{-9} M^{-2} s^{-1}

6.4 $bar^{-½}$ s^{-1}

6.6 (i) 4 times, (ii) $\frac{1}{4}$ times
6.8 (i) 4.67×10^{-3} M s^{-1} (ii) 1.92×10^{-2} s^{-1}
6.9 (i) rate = k [A] $[B]^2$ (ii) 9 times (iii) 8 times
6.10 Orders with respect to A is 1.5 and order with respect to B is zero.
6.11 Rate = k[NO_2] [F_2]
6.12 Rate law = k[A] $[B]^2$; rate constant = 6.0 M^{-2} min^{-1}
6.14 (a) 3.47×10^{-3} seconds (b) 0.35 minutes (c) 0.173 years
6.16 4.6×10^{-2} seconds
6.17 52.882 kJ mol^{-1}
6.19 1845 years
6.20 0.7842 μg and 0.227 μg

UNIT 11

11.5 6 α and 4 β
11.9 5.42 MeV
11.10 1.236×10^{13} J mol^{-1}
11.11 5.18×10^{8} years
11.12 2.3×10^{12} J
11.14 4252 years
11.22 1.82×10^{-6} g
11.24 Age 1821 years; counts 15.5 per minute.

UNIT 12

12.3 Same compounds: (a), (c) and (f).
Geometrical isomers: (b)
Structural isomers: (d), (e)
12.6 α_{obs} will be doubled. No, specific rotation will not change
12.7 * indicates chiral centre.

(i)

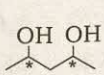
2 stereoisomers

(ii)

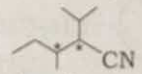
2 stereoisomers

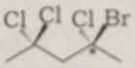
(iii)

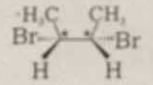
2 stereoisomers

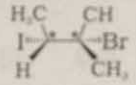
(iv) 

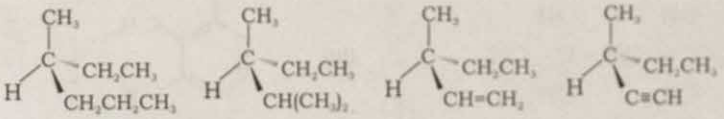
3 stereoisomers

(v)  4 stereoisomers

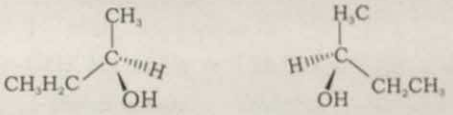
(vi)  1 stereoisomer

(vii)  3 stereoisomers

(viii)  4 stereoisomers

12.8 

12.10 (a) and (b) have *R* configuration; (c) has *S* configuration

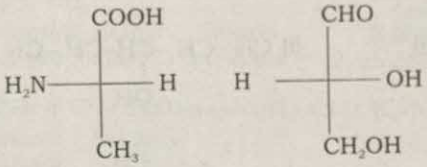
12.11 

R *S*

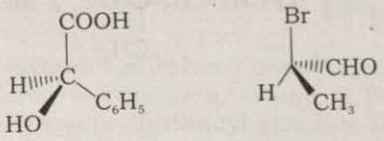
12.12 (a) and (c) : Diastereomers
(b) and (e) : Enantiomers
(d) Identical
(f) Structural isomers

12.13 (a) and (b) optically active (chiral molecules)
(c) optically inactive (centre of symmetry, achiral)

12.15 (a) Fischer projections



(b) Wedge-dash formula



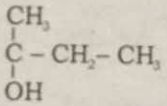
12.16 (a) and (b) : Compounds contain plane of symmetry; achiral
(c) Racemic mixture

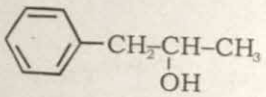
12.17 $CH_3CH_2\underset{\underset{Br}{|}}{C}HCH=CH_2$, $BrCH_2\underset{\underset{CH_3}{|}}{C}HCH=CH_2$

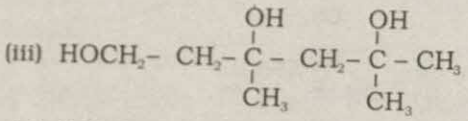
12.18 True : b, c, e, h
False : a, d, f, g

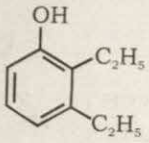
UNIT 13

13.1
(i) 2,2,4 - Trimethylpentan - 3 - ol
(ii) 5 - Ethylheptane - 2, 4 - diol
(iii) Butane -2,3 -Diol
(iv) Propane - 1,2,3 - triol
(v) 2 - Methylphenol
(vi) 4 - Methylphenol
(vii) 2,5 - Dimethylphenol
(viii) 2, 6-Dimethylphenol
(ix) 1-Methoxy-2-methylpropane
(x) Ethoxybenzene
(xi) 1 - phenoxyheptane
(xii) 2 - Ethoxybutane

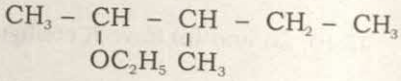
13.2 (i) 

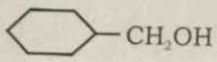
(ii) 

(iii) 

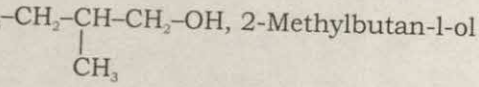
(iv) 

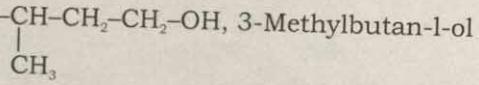
(v) $C_2H_5O - CH_2 - CH_2 - CH_3$

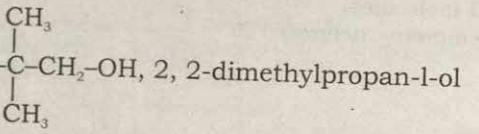
(vi) 

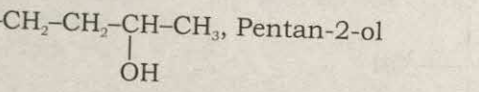
(vii) 

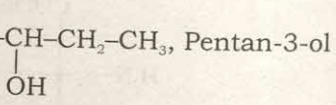
13.3 (a) $CH_3CH_2CH_2CH_2CH_2OH$, Pentan-1-ol

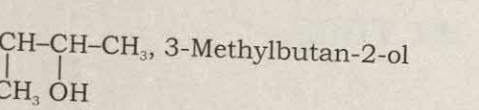
(b) 

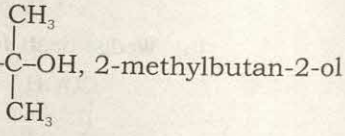
(c) 

(d) 

(e) 

(f) 

(g) 

(h) 

Primary alcohols – (a), (b), (c) and (d)
Secondary alcohols – (e), (f) and (g)
Tertiary alcohols – (h)

13.4 Hydrogen bonding in propanol

13.5 Hydrogen bonding between alcohol and water molecules.

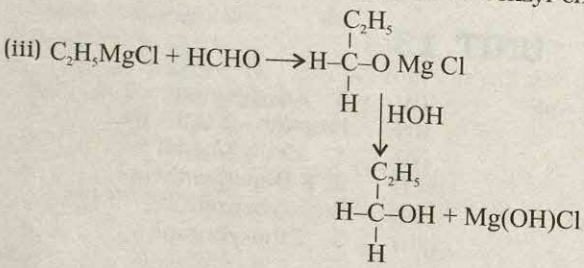
13.9 *o*-Nitrophenol is steam volatile because of intramolecular hydrogen bonding

13.12 Reaction with (i) sodium and (ii) sodium hydroxide

13.13 Due to electron withdrawing effect of nitro group and electron releasing effect of methoxy group.

13.17 (i) Hydration of Propene

(ii) By nucleophilic substitution of -Cl in benzyl chloride using dilute NaOH.

(iii) 

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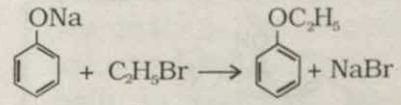
N.C.E. 2005

(iv) $CH_3MgBr + CH_3COCH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O\,Mg\,Br \xrightarrow{HOH} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + Mg(OH)Br$

13.22 (i) 2-Methy1-1-methoxypropane
(ii) 2-Chloro-1-methoxyethane
(iii) 4 - Nitroanisole
(iv) 1 - Methoxypropane

13.23 (i) $CH_3CH_2CH_2Br + CH_3CH_2CH_2ONa \longrightarrow CH_3CH_2CH_2OCH_2CH_2CH_3 + Na\,Br$
1–Bromopropane Sodium propoxide

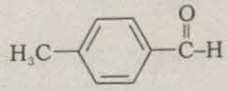
(ii) 
Sodium Phenoxide Bromo ethane

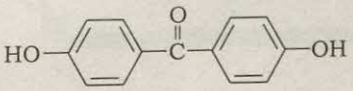
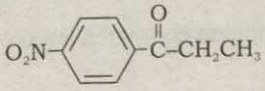
(iii) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-ONa + BrCH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OCH_3 + NaBr$
Sodium-2-methyl -2-propoxide Bromo methane 2-Methoxy -2-methyl-propane

(iv) $CH_3Br + CH_3CH_2ONa \longrightarrow CH_3OCH_2CH_3 + NaBr$
Bromo- methane Sodium- ethoxide

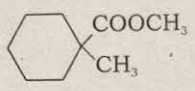
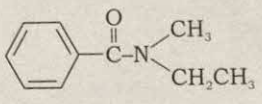
UNIT 14

14.1 (a) 4-Methylpentanal (b) But-2-enal (c) 3,3,5 trimethyl-Hexan-2-one (d) Benzene-1, 4-dicarbaldehyde (e) 6-Chloro-4-ethylhexan-3-one (f) Pentane-2, 4-dione (g) 3, 3-Dimethylbutanoic acid (h) 2, 3-Dimethylbutanoyl chloride (i) Bis-(3-methylbutanoic) anhydride (j) Isopropyl -3-phenylpropanoate (k) Propyl (3-bromophenyl) ethanoate (l) Dimethyl butanedioate (m) 2-Methylpropanamide (n) 3-Bromo-N-methylbutanamide

14.2 (a) $CH_3-\underset{CH_3}{\overset{}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H$ (b)  (c) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\underset{Cl}{\overset{}{CH}}-CH_3$

(d)  (e)  (f) $CH_3-\overset{O}{\overset{\|}{C}}-\underset{}{\overset{}{CH}}=\underset{CH_3}{\overset{}{C}}-CH_3$

(g) $CH_3-\underset{}{\overset{Br}{CH}}-\underset{C_6H_5}{\overset{}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$ (h) $CH_3C\equiv C-CH=CH-\overset{O}{\overset{\|}{C}}-OH$ (i) $CH_3-\underset{CH_3}{\overset{}{CH}}-CH_2-\underset{CH_3}{\overset{}{CH}}-\overset{O}{\overset{\|}{C}}-Cl$

(j) $H-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$ (k)  (l) 

(m) $CH_3-CH(CH_3)-\overset{O}{\overset{\|}{C}}-NHCH_3$

14.3 (b), (e), (f), (g): Aldol condensation. (a), (c), (i): Cannizzaro reaction. (d), (h): Neither.

14.6 2-Ethylbenzaldehyde (draw the structure yourselves)

14.7 (i) $CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3$, butyl butanoate

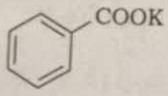
(ii) $(CH_3)_2CHCOOCH_2CH(CH_3)_2$, (2-methylpropyl) 2-methylpropanoate.

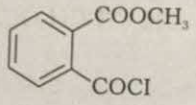
14.9 (a) Di-*tert*-butyl ketone < Methyl *tert*-butyl ketone < Acetone < Acetaldehyde

(b) $(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

(c) 2-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid

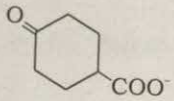
(d) $CH_3CONH_2 < CH_3COOCH_3 < (CH_3CO)_2O < CH_3COCl$

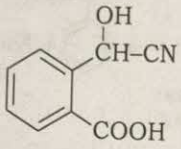
14.14 (a) 

(b) 

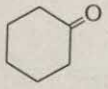
(c) $C_6H_5CH=NHNHCONH_2$

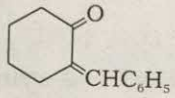
(d) $CH_3CH_2-CH(OH)-CH_2CH_3$

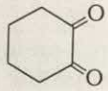
(e) 

(f) 

(g) $C_6H_5CH=C(CH_3)-CHO$ (h) $CH_3CH(OH)CH_2COOC_2H_5$ (i) $C_6H_5CH_2N(CH_3)_2$

14.15. (i) A = C_6H_5CHO B = 

C = 

D = 

(ii) E=$C_6H_5COOC_6H_5$, F=$C_6H_5CH_2OH$, G=C_6H_5OH, H=C_6H_5CHO, I=C_6H_5COONa , J=C_6H_5COCl

SCIENCE RELATED VALUES

Curiosity, quest for knowledge, objectivity, honesty and truthfulness, courage to question, systematic reasoning, acceptance after proof/verification, open-mindedness, search for perfection and team spirit are some of the basic values related to science. The processes of science, which help in searching the truth about nature and its phenomena are characterised by these values. Science aims at explaining things and events. Therefore to learn and practise science :

- Be inquisitive about things and events around you.
- Have the courage to question beliefs and practices.
- Ask 'what', 'how' and 'why' and find your answers by critically observing, experimenting, consulting, discussing and reasoning.
- Record honestly your observations and experimental results in your laboratory or outside it.
- Repeat experiments carefully and systematically if required, but do not manipulate your results under any circumstance.
- Be guided by facts, reasons and logic. Do not be biased in one way or the other.
- Aspire to make new discoveries and inventions by sustained and dedicated work.

CONSTITUTION OF INDIA

Part III (Articles 12 – 35)
(Subject to certain conditions, some exceptions and reasonable restrictions)

guarantees these

Fundamental Rights

Right to Equality

- before law and equal protection of laws;
- irrespective of religion, race, caste, sex or place of birth;
- of opportunity in public employment;
- by abolition of untouchability and titles.

Right to Freedom

- of expression, assembly, association, movement, residence and profession;
- of certain protections in respect of conviction for offences;
- of protection of life and personal liberty;
- of free and compulsory education for children between the age of six and fourteen years;
- of protection against arrest and detention in certain cases.

Right against Exploitation

- for prohibition of traffic in human beings and forced labour;
- for prohibition of employment of children in hazardous jobs.

Right to Freedom of Religion

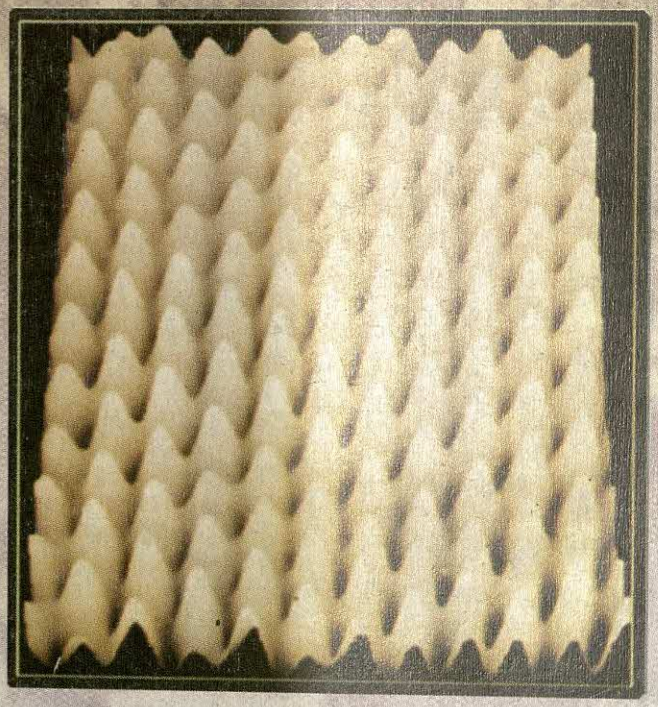
- freedom of conscience and free profession, practice and propagation of religion;
- freedom to manage religious affairs;
- freedom as to payment of taxes for promotion of any particular religion;
- freedom as to attendance at religious instruction or religious worship in educational institutions wholly maintained by the State.

Cultural and Educational Rights

- for protection of interests of minorities to conserve their language, script and culture;
- for minorities to establish and administer educational institutions of their choice.

Right to Constitutional Remedies

- by issuance of directions or orders or writs by the Supreme Court and High Courts for enforcement of these Fundamental Rights.



This micrograph which reprsents the surface of a gold specimen was taken with a sophisticated Atomic Force Microscope (AFM). Individual atoms for a crystallographic surface plane are resolved.

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NATIONAL COUNCIL OF EDUCATIONAL RESEARCH AND TRAINING

ISBN - 81-7450-19[illegible]3